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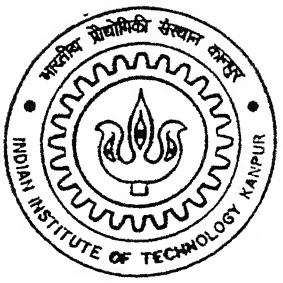
CORRELATIONSHIP BETWEEN PHYSICAL PROPERTY AND CHEMISTRY OF TOOL STEELS IN ANNEALED AND TREATED STATE

By

Jayant Jain



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DEPARTMENT OF MATERIALS AND METALLURGICAL ENGINEERING

Indain Institute of Technology Kapnur

JUNE, 2004

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In Partial Fulfillment of the Requirements
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by

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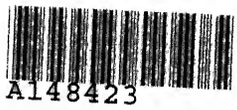

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Certificate

*It is certified that the work contained in the thesis titled "**Correlationship between physical property and chemistry of tool steels in annealed and heat treated state**" by Mr. Jayant Jain has been carried out under our supervision and it has not been submitted elsewhere for a degree.*

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ABSTRACT

The driving force for current research is ambiguity in understanding certain physical properties of tool steels with respect to their chemistry. The aim of this work is to give an insight about the physical properties of tool steels with respect to their chemistry. Among various physical properties present study deals with density, Elastic properties (E, G, and υ) and specific heat. The main aim of this work is to clarify the role of alloying elements on basic physical properties of tool steels. There is no proper correlationship between physical properties and chemistry of tool steels. For the first time, the present study sheds some light on the shear modulus and Poisson's ratio of high alloy tool steels. These properties have so far not been reported in the accessible literature. This work is the first study which distinguishes systematically physical properties in the annealed state from those in the hardened and tempered condition. In this study, the densities of conventional and powder metallurgical tool steels were measured at room temperature using Archimedes' principle. The heat capacities of selected conventional and powder metallurgical tool steels were determined as a function of temperature using differential scanning calorimetry (DSC). In the present study, the elastic properties were measured using ultrasonic pulse echo technique. In order to clarify the effect of heat treatment on physical properties and their correlationship with chemistry, physical properties were separately measured and correlated with chemistry of tool steels in annealed and heat treated condition. For correlation purpose, a multilinear regression analysis is used. The final aim of this work is to determine the suitable mathematical relationship between physical properties and chemistry of tool steels in annealed and heat treated state separately. So that, we can find out these properties of other chemically known tool steels in annealed and heat treated state.

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Kanpur, 31st May 2004 Jayant Jain

Chapter 1

INTRODUCTION

Tool steels have been developed empirically over many centuries and are often tailored for specific applications. Tool steels are iron based alloys typically with additions of chromium, molybdenum, vanadium or tungsten to combine with high levels of carbon to form carbide particles which impart outstanding wear and erosion resistance. The alloying elements also contribute to strengthening of the base material as well as some degree of corrosion resistance depending upon specific composition. Maximum properties are obtained by heating to elevated temperature to re-solution alloying elements (austenitizing step), followed by rapid cooling in air, water or oil depending on grade (quenching step), and then a low temperature treatment to partially soften the product to impart a degree of ductility and toughness (tempering step). Sometimes a sub-zero or cryogenic treatment is employed prior to tempering to enhance hardening response or dimensional stability. Tool steels are used for certain kinds of hand tools and in equipment for cutting, shaping, forming, blanking, and drilling of materials at ambient or elevated temperature. Most tool steels are used in a heat-treated state, generally hardened and tempered [1]

Tool steels are classified into several broad groups, some of which are further divided into subgroups according to alloy composition, hardenability, or mechanical similarities.

Water-hardening, or carbon, tool steels:

Designated Type W by AISI; rely solely on carbon content for their useful properties. These steels are available as shallow, medium, or deep hardening, so the specific alloy selected depends on part cross section and required surface and core harnesses.

Shock-resisting tool steels (Type S):

Shock resisting tool steels are strong and tough, but they are not as wear resistant as many other tool steels. These steels resist sudden and repeated

loadings. Applications include pneumatic tooling parts, chisels, punches, shear blades, bolts, and springs subjected to moderate heat in service.

Cold-work tool steels:

Which include oil and air-hardening Types O, A, and D, are often more costly but can be quenched less drastically than water-hardening types. Type O steels are oil hardening; Type A and D steels are air hardening (the least severe quench), and are best suited for applications such as machine ways, brick mold liners, and fuel-injector nozzles. The air-hardening types are specified for thin parts or parts with severe changes in cross section that are prone to crack or distort during hardening. Hardened parts from these steels have a high surface hardness; however, these steels should not be specified for service at elevated temperatures.

Hot-work steels (Type H):

Serve well at elevated temperatures. The tungsten and molybdenum high-alloy hot-work steels are heat and abrasion resistant even at 600 to 1,000°F. But although these alloys do not soften at these high temperatures, they should be preheated before and cooled slowly after service to avoid cracking. The chromium grades of hot-work steels are less expensive than the tungsten and molybdenum grades. One of the chromium grades H11 is used extensively for aircraft parts such as primary airframe structures, cargo-support lugs, catapult hooks, and eleven hinges. Grade H13, which is similar to H11 is usually more readily available from suppliers.

High-speed tool steels:

High speed steels (HSS) are basically a group of iron base alloys containing some 20-30% of mainly carbide forming alloying elements and can be hardened to a level of up to 65-70% HR_C, and that no appreciable softening takes place until temperatures in the region of 600°C are reached. The microstructure consists of tough tempered martensite matrix with a dispersion of wear resistance, high hardness alloy carbides [2-6]. T (tungsten alloy) and M (molybdenum alloy) make

good cutting tools because they resist softening and maintain a sharp cutting edge at high service temperatures. This characteristic is sometimes called "red hardness." These deep-hardening alloys are used for steady, high-load conditions rather than shock loads. Typical applications are pump vanes and parts for heavy-duty strapping machinery [7].

Other grades, called special-purpose tool steels, include low-cost, Type L, low-alloy steels, often specified for machine parts when wear resistance combined with toughness is important. Carbon-tungsten alloys (Type F) are shallow hardening and wear resistant, but are not suited for high temperatures or for shock service [8].

Almost, all properties of tool steels are driven by their alloying elements. So, complete knowledge on the properties of these tool steels with respect to their chemistry is very important. The inclusion of alloying elements in steels gives a multitude of physical properties to steels depending upon number of alloying elements added and their alloying content. There are certain physical properties of tool steels, which are not very well documented with respect to their alloying elements. These properties are density, elastic properties, specific heat, thermal conductivity and thermal diffusivity. The data on these properties is scarce. There is no proper correlationship between physical properties and chemistry of tool steels. The main reason for bad correlation are discrepancies between different sources and lack of information on the status of heat treatment. The data on physical properties of tool steels seems to be more guessed than measured.

Chapter 2 overviews the existing literature on physical properties of tool steels with emphasis on density, elastic properties and heat capacity of tool steel. There is not a wealth of information available in the literature about these physical properties. This chapter covers first, brief description of basic physical property (density, elastic property and specific heat), followed by literature review and finally brief idea about heat treatment of tool steels.

Chapter 3 covers the scope of the current research while; chapter 4 describes in detail the experimental procedures. It includes brief introductions about measurement technique (Ultarsonic transmission technique and specific heat measurement) followed by their measurement procedure.

Chapter 5 describes the experimental results and discussions. Chapter 6 and 7 consist of conclusions and future work respectively.

Chapter 2

BACKGROUND

2.1 Introduction to basic physical property

Among various physical properties, present study deals with density, elastic properties such as elastic modulus, shear modulus, Poisson's ratio and specific heat of tool steels. These properties can be defined as follows: -

Density: Density ρ_v can be described as a gravitational property; it is defined as mass per unit volume (Eq. 2.1)

$$dm = \rho_v dV. \qquad 2.1$$

The specific volume is defined as (Eq. 2.2)

$$v = \frac{1}{\rho_v} \qquad 2.2$$

Densities of solid materials range from < 0.1g/cm³ for light polymer foams to > 20 g/cm³ for the platinum group metals [9].

Young's Modulus: Young's Modulus or elastic modulus E is the slope of the stress σ (field intensity) - strain ε (response variable) curve in the elastic regime for an elastic-plastic material (Eq. 2.3) (Figure 2.1),

$$d\sigma = E\, d\varepsilon. \qquad 2.3$$

Elastic moduli range from 100N/m² (< 200psi) for soft vinyl plastics to > 0.6×10^{12} (93Mpsi) for tungsten carbide.

On an atomic scale, macroscopic elastic strain is manifested as small changes in the interatomic spacing, and stretching of interatomic bonds. For covalently bonded materials the elastic modulus is therefore a measure of the resistance to

bond stretching from the equilibrium separation r_0. This modulus is proportional to the slope of the interatomic force-separation curve (Figure 2.2) at the equilibrium spacing,

$$E \propto \left(\frac{dF}{dr}\right)_{r_0}. \qquad 2.4$$

the smaller the radius of curvature in the bond energy well, i.e., the steeper the walls of the potential energy well, the larger is the amount of energy to displace atoms from their equilibrium positions; the higher is the elastic modulus [9].

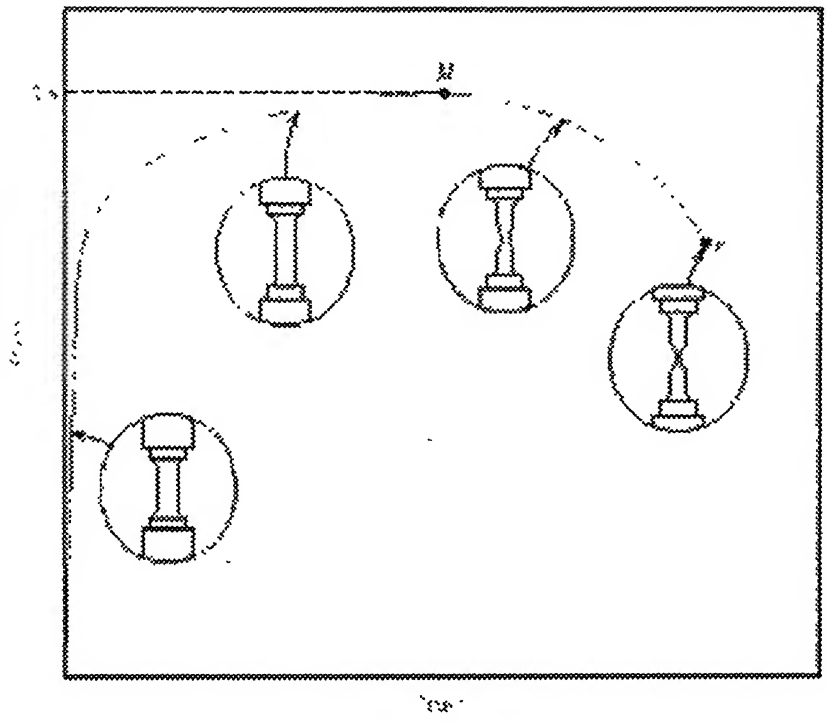

Figure. 2.1: Typical engineering stress-strain behaviour to fracture, point F. The tensile strength is indicated at point M. The circular insets represent the geometry of the deformed specimen at various points along the curve [9].

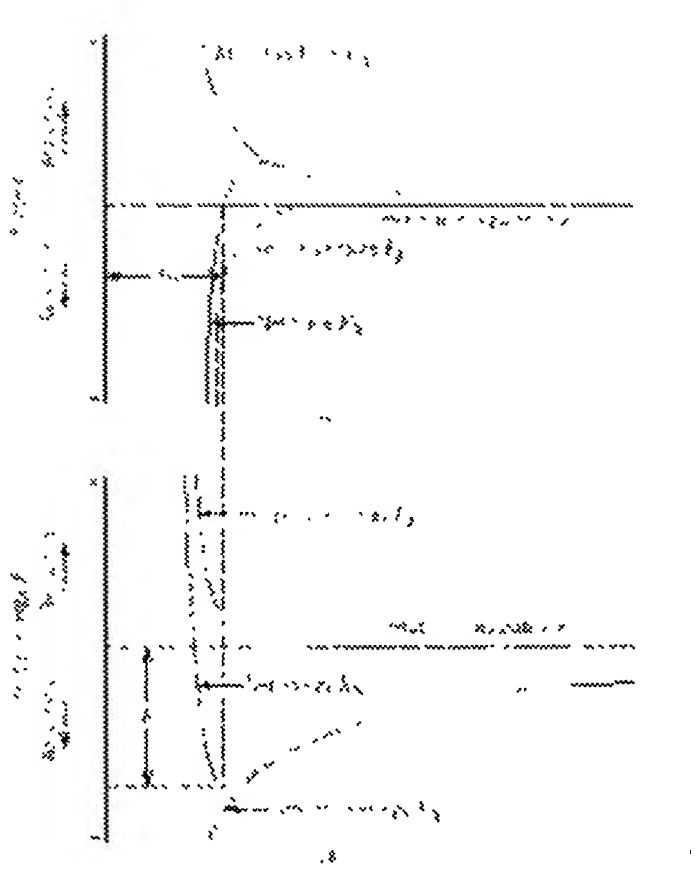

Figure 2.2: (a) The dependence of repulsive, attractive, and net force on interatomic separation for two isolated atoms. (b) The dependence of repulsive, attractive, and net potential energies on interatomic separation for two isolated atoms [9].

Shear Modulus: Shear Modulus of Elasticity is similar to the ratio of stress to strain in a material subjected to shear stress (Eq. 2.5),

$$\sigma_{xy} = G\gamma_{xy}, \qquad 2.5$$

where σ_{xy} is the shear stress (force in X direction, applied to an area with its normal in the y direction) and γ_{xy} is the shear strain (dx/dy) [9].

Poisson's Ratio: Poisson's Ratio is the ratio of transverse strain to corresponding axial strain on a material stressed along one axis (Eq. 2.6) (Figure 2.3),

$$\sigma = \frac{transverse\ strain}{longitudnal\ strain}$$

$$= \frac{\Delta D/D}{-\Delta L/L} \qquad 2.6$$

Specific heat: The amount of heat required to raise the temperature of a given body through a given interval; varies from body to body. If the heat ΔQ given to a body can increase the temperature of that body through ΔT then the heat capacity of the body is

$$\text{Heat capacity} = \Delta Q / \Delta T$$

The heat capacity per unit mass of the body is called specific heat capacity.

$$C = \Delta Q/m.\Delta T$$

If m =1, $\Delta t = 1^0C$ then C = ΔQ. Thus, specific heat can also be defined as the amount of heat required to raise the temperature of unit mass of the substance through unit interval.

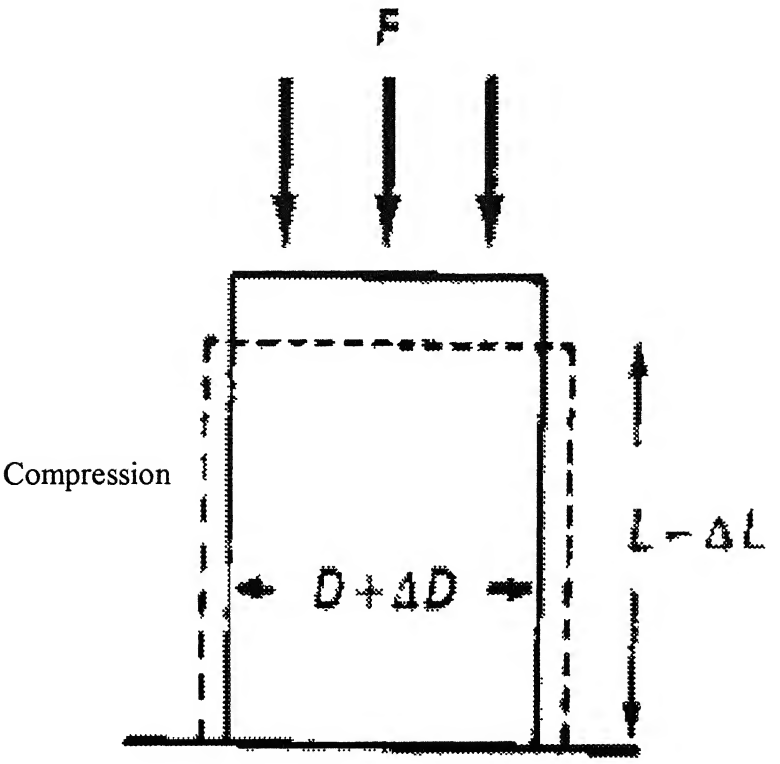

Figure 2.3: Solid block under compression [9].

2.2 Literature review

Tool steels have been known for about a century, during which time there have been many developments to keep pace with increasing demands on properties and with advances in basic metallurgical understanding. Tool steels are amongst the most important engineering materials. Physical properties of tool steels are not documented systematically in literature with respect to their chemistry. Data available are very scarce. There is no distinction of physical property between annealed and heat trated state.

Density of tool steels depends upon type and amount of alloying elements. Figure 2.4 was an attempt to correlate the density data of conventional and powder metallurgical tool steels with chemical composition. W and Mo add to density, V and Cr reduces the density, statistically Co has no effect. Reliability is not convincing, partially because of systematic differences between annealed and fully heat treated state, which is usually not mentioned in most of the places [10].

There is not a wealth of information in the literature on the variation of elastic properties with chemistry of tool steels. Figure 2.5 was an attempt to correlate the elastic properties of both conventional and powder metallurgical HIPed tool steels at room temperature. As is clear from this figure, there are huge discrepancies. These discrepancies represent full scatter band. The main reason for bad correlation is discrepancies between different sources and lack of information on the status of heat treatment [10].

Another very important physical property i.e. specific heat of tool steels is not very well documented. Data on the specific heat of tool steels are scarce; product information from manufacturers is usually not based on measurements. Figure 2.6 was an attempt to correlate specific heat with chemistry of tool steels. In ferritic steels, the specific heat does generally not vary to a greater extent with the composition. In carbide rich tool steels with their high alloy content the chemistry seems to be a decisive parameter. With precipitation hardening tool steels, specific heat must also be function of the heat treatment condition; yet, nothing is known about the differences between annealed and quenched and tempered state [10].

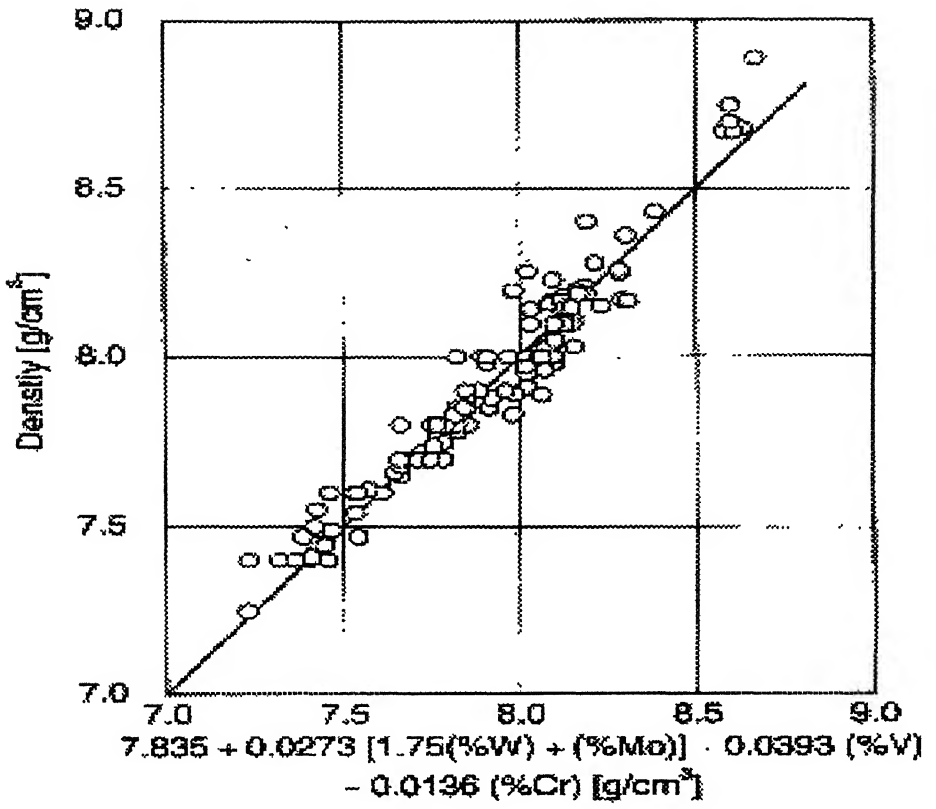

Figure. 2.4: Effect of chemical composition of conventional and powder metallurgical hot working, cold working, high speed and corrosion resistant tool steels on room temperature density [10].

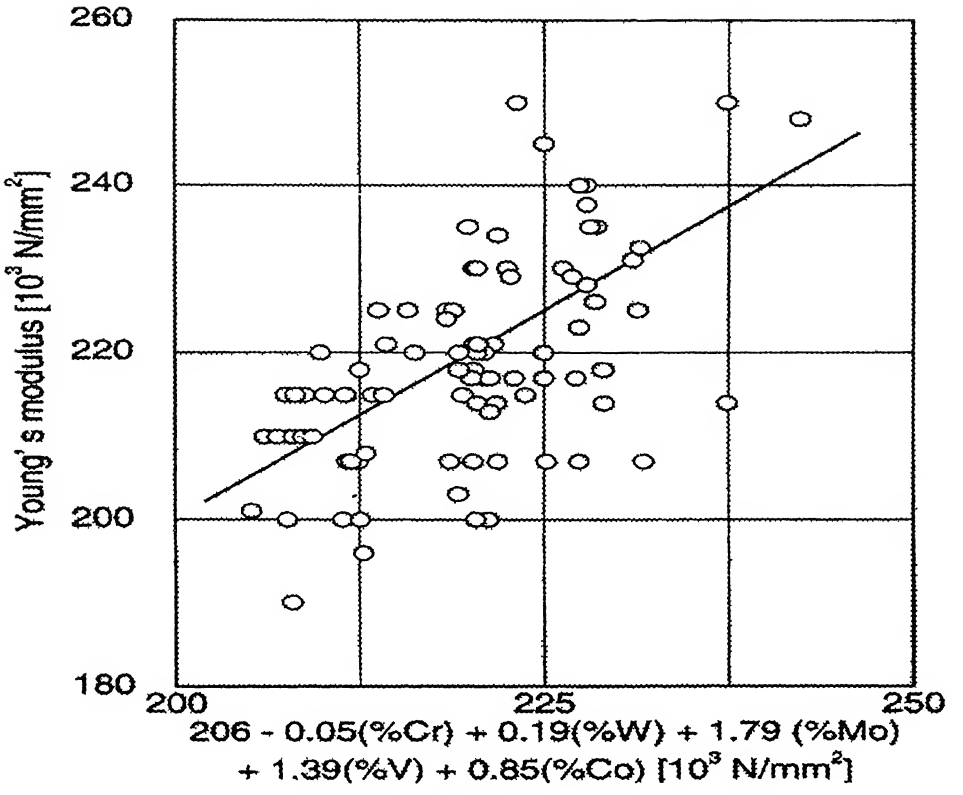

Figure 2.5: Effect of alloying elements in conventional and HIP tool steels on Young's modulus [10].

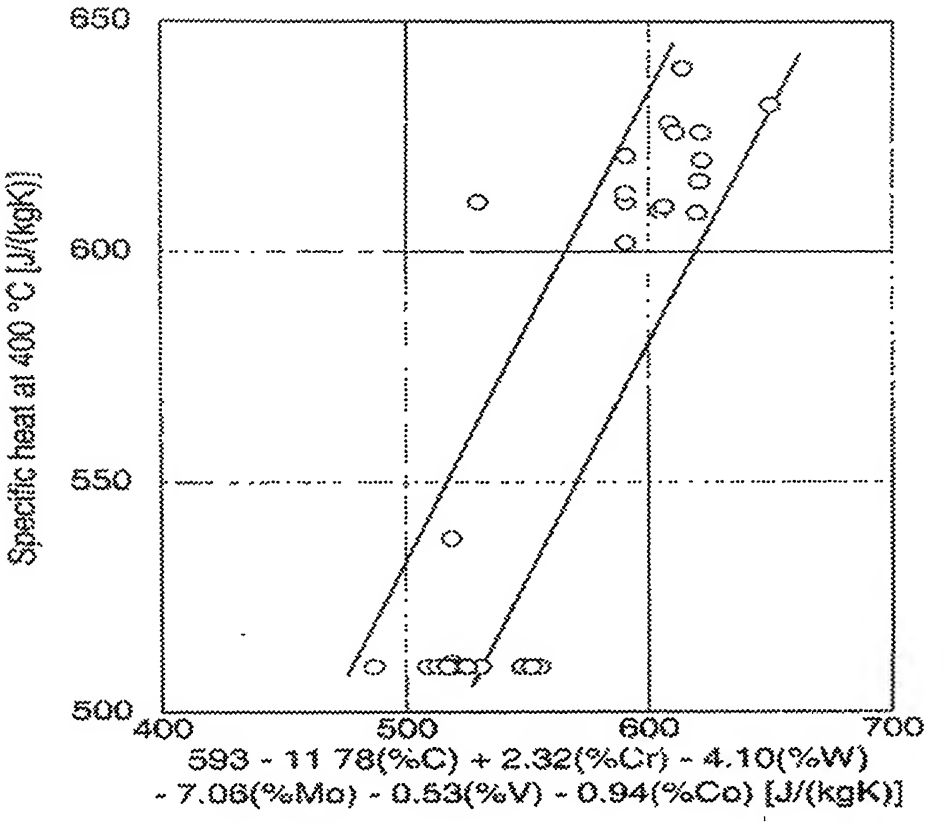

Figure 2.6: Influence of chemical composition on true specific heat of conventional and HIP hot working, cold working, corrosion resistant and high speed tool steels [10].

2.3 Heat treatment of tool steels

Heat treatment is the controlled heating and cooling of metals to alter their physical and mechanical properties without changing the product shape.

For a tool steel to perform effectively a component when machined will usually require heat treatment. This will enable the tool to develop the characteristic properties required for a high hardness with good wear, abrasion and impact values, which vary with each specification. For heat treatment a tool steel component requires preheating (to avoid cracking and unnecessary distortions of the component), then it is raised to its final hardening temperature. An important point is the great necessity of having the tool steel uniformly heated through or as generally termed "well soaked". To achieve a high hardness the steel then requires rapid cooling. The name given to this process is "QUENCHING". Dependant on specification the steel may be quenched in oil or cooled in air or inert gas or in salt bath. After quenching some austenite will be retained which necessitates to temper the steel without longer delays to prevent austenite stabilization. To make use of precipitation hardening potential the tempering takes place at temperatures exceeding 500°C to allow the metallic alloying elements to diffuse. During tempering, retained austenite loses some of its carbon and alloy content to the carbidic precipitates and can transform to martensite on cooling below 500°C. To temper also this secondary martensite, at least a second tempering is necessary; three tempering cycles are common [17].

Most tools and dies must be protected from oxidation and decarburisation during treatment. The heat treaters use four basic types of furnaces with various processing media to meet this requirement:

- **Salt baths:** The traditional route capable of treating the complete range of tool steels with tight control.
- **Fluidised beds:** A more recent development capable of treating a wide range of tool steels other than those requiring high hardening temperatures.
- **Sealed-quench furnaces:** Applications restricted by lower hardening temperatures and the choice of oil quenching or "still" gas cooling.
- **Vacuum furnaces:** The cleanest route, mainly employing gas quenching; the recent introduction of high-pressure gas quenching has widened the range of steels, which can be successfully treated [11].

In the present study, heat treatments of conventional and PM HIPed tools were carried out in salt bath furnaces at OTTO FUCHS, Meinerzhagen, Germany.

Chapter 3

SCOPE OF THE PRESENT WORK

In this investigation, measurements of densities were carried out in annealed and heat treated state. Density measurements were based on Archimedes principle. The density measurement has three purposes; first to see its correlation with alloying elements in annealed and heat treated state. Secondly, to calculate elastic properties and thirdly, to see the relationship between density change ($\Delta\rho$) from annealed to hardened and tempered condition with hardness (HRC).

Hardness in tool steels is most commonly measured using the Rockwell C method. In present investigation hardness of tool steels in hardened and tempered condition were measured using Rockwell C method. The measured hardness values were correlated with density change. There should be some relationship between density change ($\Delta\rho$) from annealed to hardened condition and hardness (HRC) in conventional and powder metallurgical tool steels.

The ultrasonic researches allow obtaining full and reliable information about physical properties of different systems. Ultrasonic technique is not only used to detect voids, cracks, inclusions, precipitates, etc., but also applicable for material characteristics evaluation. Acoustic velocity and attenuation are commonly used for such purposes. Acoustic velocity of an ultrasonic wave as it propagates through solid material is affected by elastic modulus (E), density (ρ) and Poisson's ratio (υ). The material properties (such as E, G, υ), which are of interest in many manufacturing and research applications, can be determined quickly and easily through computations based on sound velocities. Sound velocity can be easily measured using ultrasonic pulse-echo techniques [11-12]. In present study, the velocity data together with measured densities were used to calculate the elastic properties: Young's modulus (E), shear modulus (G), and Poisson's ratio (υ).

Measurements of specific heat of substances by differential scanning calorimetry are a very well known technique [13-16]. In present study DSC technique is used for the determination of heat capacities of selected tool steels in annealed and heat treated condition. The measurements of specific heats were carried out upto 800°C in argon atmosphere. The main aim of determination is to correlate

specific heat with chemistry of tool steels. Also, to see if heat treatment makes any difference on dependence of heat capacity of tool steels with alloying chemistry.

Improved knowledge on above mentioned physical properties of tool steels with respect to chemistry helps to optimise alloy and processing design, especially when new requirements for processing advanced materials arises.

The driving force for current research is ambiguity in understanding these properties with respect to chemistry of tool steels. This work mainly concentrates on density, elastic properties and specific heat measurements in conventional and powder metallurgical tool steels. In order to clarify the role of heat treatment each property is separately measured and correlated with chemistry of tool steels in annealed and heat treated condition. For correlation purpose a multilinear regression analysis is used.

The final aim of this work is to prognosticate the suitable mathematical relationship between these properties and composition of tool steels in annealed and heat treated state separately. So that we can find out the important physical properties (ρ, E, G, ν and C_p) for other tool steels.

Chapter 4

EXPERIMENTAL PROCEDURE

The present chapter deals with chemistry of selected tool steels for physical property measurement and their heat treatments. This chapter also covers the measurement procedure used for physical property (density, elastic property and heat capacity) measurement.

4.1 Chemistry of tool steels

Many different compositions of tool steels are selected for present study. Tool steels ranging from high alloy content to low alloy content, conventional to powder metallurgical, all are incorporated in present study. The idea behind this is to see the effect of each alloying elements on elastic properties and heat capacity of tool steels in annealed and heat treated condition. An overview on chemistry of selected tool steels is given in the table 4.1. Beyond the elements listed, all steels contain, as usually 0.3-0.9% Si and 0.3-0.7%Mn.

Table 4.1: Chemical compositions of selected conventional and PM HIPed tool steels for elastic properties measurement in wt %.

Tool steel Grade	Type	C	Cr	Mo	V	W	Co	Ni	Nb
1.2343 [1]	Conventional	0.39	5.15	1.25	0.37	-	-	0.12	-
1.2344 [1]	Conventional	0.40	5.15	1.35	1.00	-	-	-	-
1.2367 [2]	Conventional	0.37	4.95	2.87	0.55	-	-	0.17	-
101≈2343 [2]	Conventional	0.29	5.01	1.91	0.46	-	-	0.12	-
TSP 8-18Cr [2]	PM HIPed	2.97	17.50	2.90	8.23	-	-	0.28	1.77
CPM 3V [1]	PM HIPed	0.80	7.50	1.30	2.75	-	-	-	-
CPM 10V [1]	PM HIPed	2.45	5.25	1.30	9.75	-	-	-	-
CPM 15V [1]	PM HIPed	3.40	5.25	1.30	14.5	-	-	-	-
CPM Re X M4 [1]	PM HIPed	1.30	4.00	4.50	4.00	5.50	-	-	-
CPM M4 [1]	PM HIPed	1.30	4.00	4.50	4.00	5.50	-	-	-
CPM T15 [1]	PM HIPed	1.60	4.00	-	4.90	12.00	5.00	-	-
1.3343 [2]	PM HIPed	0.93	3.93	4.88	1.85	6.12	-	0.32	-
1.3344 [2]	PM HIPed	1.24	3.90	4.83	2.73	6.12	0.29	0.37	-
TSP 23 [2]	PM HIPed	1.29	4.08	4.88	3.08	6.48	0.21	-	-
TSP 8 [2]	PM HIPed	2.42	6.24	3.50	7.75	0.38	-	-	1.79
TSP 5 [2]	PM HIPed	1.61	4.75	2.17	4.99	10.06	7.65	0.23	-
TSP 4 [2]	PM HIPed	1.33	3.86	4.36	3.83	5.32	-	-	-

Table 4.1: Continued

ESP 4 [2]	Spray formed	1.29	3.97	5.06	4.23	5.93	0.51	0.22	-
TSP 1 [2]	PM HIPed	0.79	6.24	3.01	1.19	0.31	3.24	0.14	0.84
TSP 30 [2]	PM HIPed	1.29	4.23	4.94	3.01	6.51	8.12	0.29	-
1.3247 [2]	PM HIPed	1.07	3.90	9.20	1.21	1.40	7.80	0.13	-
1.3243 [2]	Conventional	0.91	4.10	4.80	1.80	6.10	4 90	0.23	-
ASP 30 [1]	PM HIPed	1.28	4.20	5.00	3.10	6.40	8.50	-	-
T 15 HIP [1]	PM HIPed	1.50	4.60	0.90	5.00	13.0	4.80	-	-
1.2888 [1]	Conventional	0.20	9.50	2.00	-	5.50	10.0	-	-
1.2889 [1]	Conventional	0.45	4.50	3.05	1.95	-	4.50	-	-
1.2379 [2]	Conventional	1.52	11.23	0.75	0.83	-	-	-	-
1.2999 [2]	PM HIPed	0.42	3.07	4.97	0.94	-	-	0.22	-
ESP 23 [2]	Spray formed	1.54	8.85	2.07	2.10	0.19	0.12	0.17	1.01
ESP 32 [2]	Spray formed	1.80	3.89	3.93	4.69	9.26	9.84	0.12	1.24
1.2365 [1]	Conventional	0.31	2.95	2.80	0.55	-	-	-	-
Micro-Melt M4 [1]	PM HIPed	1.35	4.50	4.50	4.00	5.50	-	-	-
Micro-Melt 23 [1]	PM HIPed	1.25	4.10	4.95	3.00	6.25	-	-	-
Micro-Melt 30 [1]	PM HIPed	1.27	4.20	5.00	3.10	6.25	8.12	0.29	-
Micro-Melt A 11 LVC [1]	PM HIPed	1.78	5.25	1.30	8.88	-	-	-	-
Micro-Melt A 11 [1]	PM HIPed	2.45	5.25	1.30	9.75	-	-	-	-

T 15 spray formed [2]	Spray formed	1.53	3.92	0.86	5.06	11.60	4.43	-	-

1: Nominal chemical composition

2: Analysed chemical composition

Measurements of specific heat were carried out on five selected tool steels The chemical composition of selected tool steels is given in table 4.2. Beyond the elements listed, all steels contain, as usually 0.3-0.9% Si and 0.3-0.7%Mn. The selected samples include tool steels of low alloy to high alloy content. The idea behind the selection is to see the effect of chemistry on specific heat of tool steels in annealed and heat treated state.

Table 4.2: Chemical compositions of selected tool steels for specific heat measurements in wt %.

Tool steel grade	Type	C	Cr	Mo	V	W	Co	Ni	Nb
1.2766 [2]	Conventional	0.34	1.76	0.38	0.02	-	-	3.86	-
1.3247 [2]	PM HIPed	1.07	3.90	9.20	1.21	1.40	7.80	0.13	-
1.3243 [2]	Conventional	0.91	4.10	4.80	1.80	6.10	4.90	0.23	-
TSP 30 [2]	PM HIPed	1.29	4.23	4.94	3.01	6.51	8.12	0.29	-
ESP 32 [2]	Spray formed	1.80	3.89	3.93	4.69	9.26	9.84	0.12	1.24

1: Nominal chemical composition

2: Analysed chemical composition

4.2 Salt Bath Heat Treatment

In the present investigation the heat treatment of all the selected conventional and PM tool steels were carried out in salt bath furnace. As the name implies this type of processing is carried out using baths of different salt mixes with different melting points. The salts are melted in a heat resistant pot and once fluid they are available as a heating medium. As a hot liquid it exhibits a natural convection and hence has good temperature uniformity and ease of control of temperature by immersion thermocouples. Having various furnaces in various temperature ranges give the versatility associated with salt bath processing. Individual furnace temperatures can be adjusted to suit requirements and the items are manually moved from furnace to furnace. Having achieved the hardening temperature the jobs are removed and quenched as required. The quenching medium, being separate from the heating furnaces can be whatever is required for that individual process e.g. air, salt, oil or water.

A typical salt bath heat treating cycle is schematically shown in Figure 4.1 with two holding times during heating to austenitizing temperature, a salt bath quench and a triple tempering treatment. In present study 1^{st} and 2^{nd} preheating were carried out in air and salt bath respectively. The furnaces used for preheating are shown in Figure 4.2 (a) and (b). Heating up to austenitizing was achieved in a salt bath furnace as shown in Figure 4.3. All the samples were tempered in salt bath as shown in Figure 4.4.

After processing, the items are covered with a layer of salt and therefore cleaning needs to be carried out i.e. washing and blasting.

The main parameters of heat treatment for each sample are summarised in table 4.3.

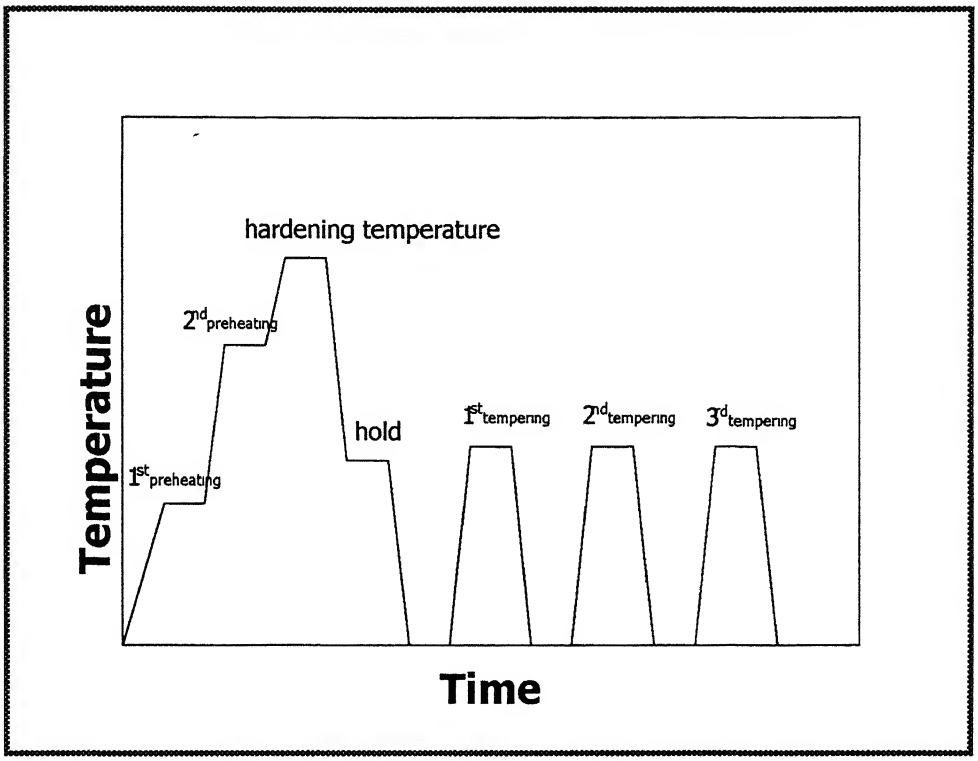

Figure 4.1: Typical heat treating cycle for high alloy conventional and powder metallurgical tool steels comprising two holding times during preheating, salt bath quench and triple tempering.

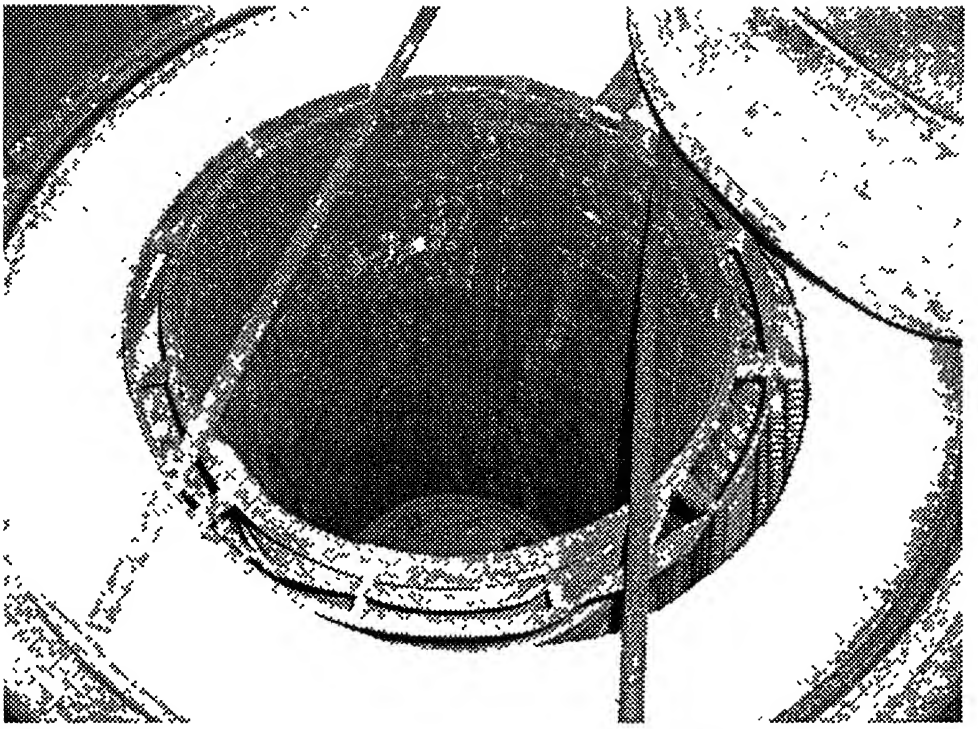

Figure 4.2(a): Preheating furnace upto 400°C in air.

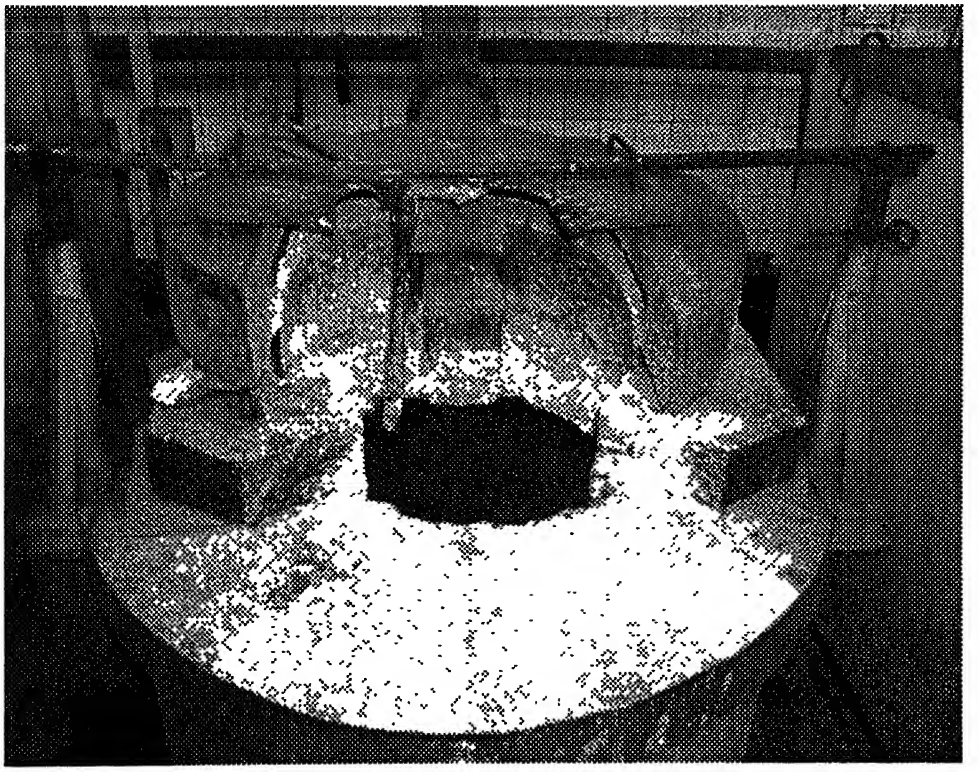

Figure 4.2(b): Salt bath preheating furnace upto 900°C.

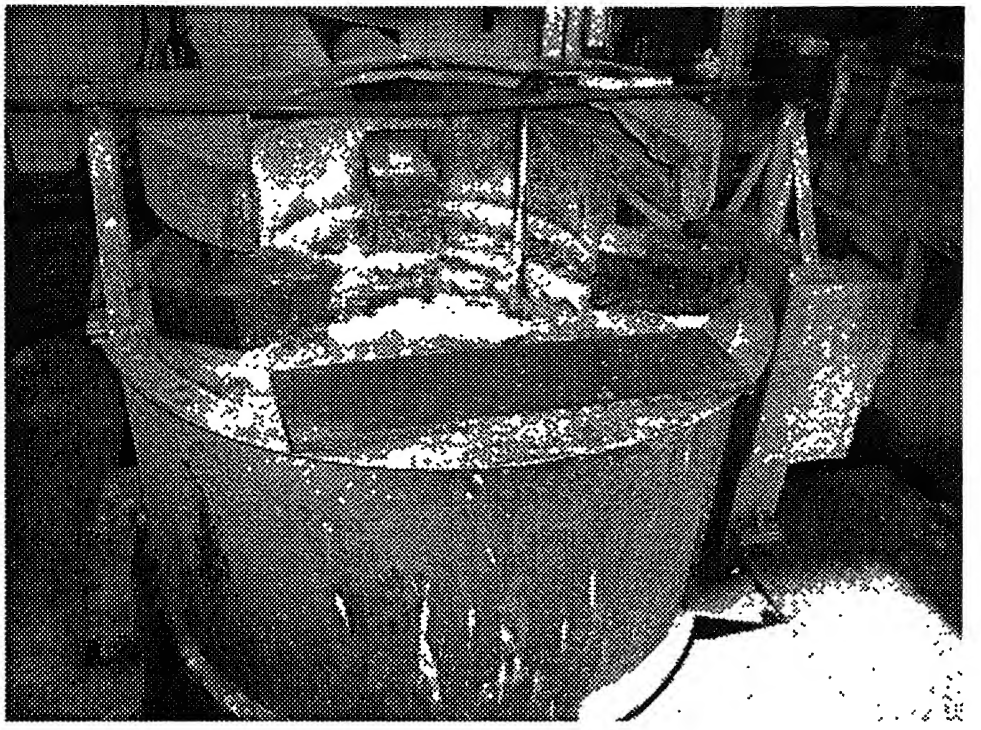

Figure 4.3: Salt bath hardening furnace upto 1200°C.

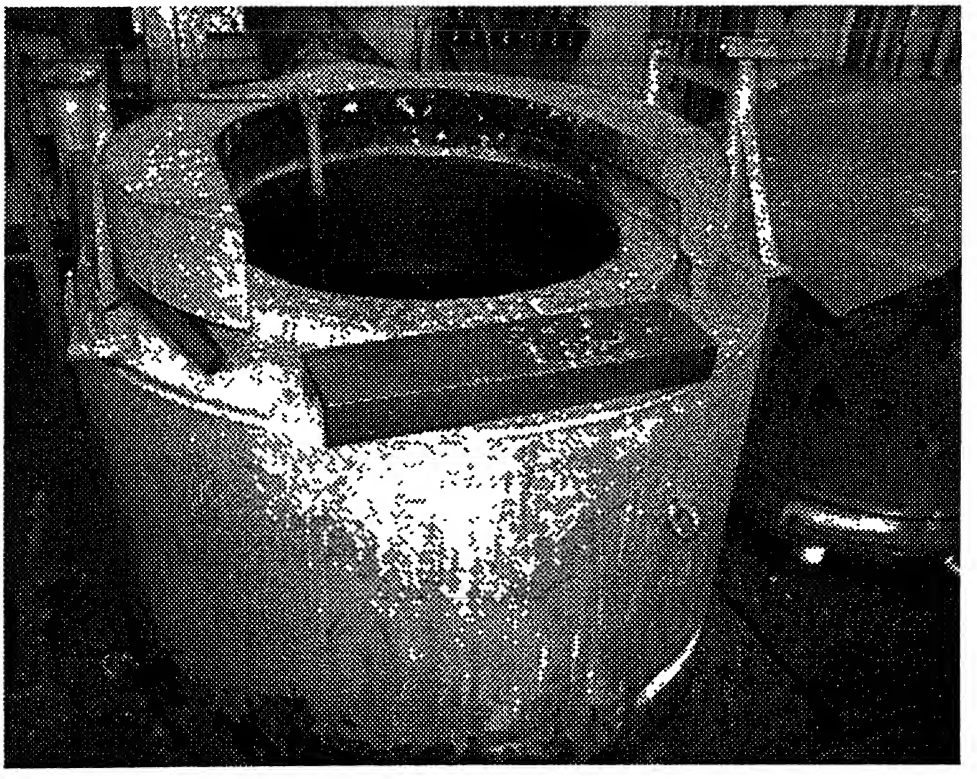

Figure 4.4: Salt bath tempering furnace upto 650°C.

Table 4.3: Heat treatment parameters and hardness (HRC) for conventional and powder metallurgical tool steels.

Steel grade	Heat treatment parameters		Hardness (HRC)
1.2343	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1010°C in salt ($BaCl_2$+MgF_2) 2×2h at 580°C ($BaCl_2$)	47
1.2344	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1010°C in salt ($BaCl_2$+MgF_2) 2×2h at 580°C ($BaCl_2$)	50
1.2367	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1040°C in salt ($BaCl_2$+MgF_2) 2×2h at 580°C ($BaCl_2$)	53
1.2365	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1040°C in salt ($BaCl_2$+MgF_2) 2×2h at 580°C ($BaCl_2$)	52
101≈2343	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1000°C in salt ($BaCl_2$+MgF_2) 3×2h at 580°C ($BaCl_2$)	46
1.2766	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$+MgF_2) 1×2h at 180°C ($BaCl_2$)	48
CPM 3V	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1070°C in salt ($BaCl_2$+MgF_2) 3×2h at 520°C ($BaCl_2$)	59

Table 4.3: Continued

CPM 10V	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1050°C in salt ($BaCl_2$+MgF_2) 3×2h at 540°C ($BaCl_2$)	63
CPM 15V	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1050°C in salt ($BaCl_2$+MgF_2) 3×2h at 540°C ($BaCl_2$)	64
CPM Re X M4	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1180°C in salt ($BaCl_2$+MgF_2) 3×2h at 560°C ($BaCl_2$)	65
CPM T15	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1180°C in salt ($BaCl_2$+MgF_2) 3×2h at 540°C ($BaCl_2$)	67
1.3343	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1190°C in salt ($BaCl_2$+MgF_2) 3×2h at 540°C ($BaCl_2$)	65
1.3344	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1190°C in salt ($BaCl_2$+MgF_2) 3×2h at 540°C ($BaCl_2$)	66
TSP 23	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1100°C in salt ($BaCl_2$+MgF_2) 3×2h at 560°C ($BaCl_2$)	61
TSP 8	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1050°C in salt ($BaCl_2$+MgF_2) 3×2h at 540°C ($BaCl_2$)	60

Table 4.3: Continued

TSP 5	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1150°C in salt ($BaCl_2$+MgF_2) 3×2h at 540°C ($BaCl_2$)	66
TSP 4	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1100°C in salt ($BaCl_2$+MgF_2) 3×2h at 560°C ($BaCl_2$)	60
ESP 4	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1100°C in salt ($BaCl_2$+MgF_2) 3×2h at 560°C ($BaCl_2$)	58
TSP 1	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1150°C in salt ($BaCl_2$+MgF_2) 3×2h at 560°C ($BaCl_2$)	67
TSP 30	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1170°C in salt ($BaCl_2$+MgF_2) 3×2h at 560°C ($BaCl_2$)	66
1.3247	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1190°C in salt ($BaCl_2$+MgF_2) 3×2h at 540°C ($BaCl_2$)	67
1.3243	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1190°C in salt ($BaCl_2$+MgF_2) 3×2h at 540°C ($BaCl_2$)	65
ASP 30	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1170°C in salt ($BaCl_2$+MgF_2) 3×2h at 560°C ($BaCl_2$)	65

Table 4.3: Continued

T 15 HIP	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1180°C in salt ($BaCl_2$+MgF_2) 3×2h at 540°C ($BaCl_2$)	62
1.2888	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1140°C in salt ($BaCl_2$+MgF_2) 2×2h at 680°C ($BaCl_2$)	49
1.2889	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1140°C in salt ($BaCl_2$+MgF_2) 2× 2h at 640°C ($BaCl_2$)	45
1.2379	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1080°C in salt ($BaCl_2$+MgF_2) 3×2h at 540°C ($BaCl_2$)	58
1.2999	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1070°C in salt ($BaCl_2$+MgF_2) 2×2h at 560°C ($BaCl_2$)	54
ESP 23	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1080°C in salt ($BaCl_2$+MgF_2) 3×2h at 560°C ($BaCl_2$)	58
ESP 32	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1180°C in salt ($BaCl_2$+MgF_2) 3×2h at 560°C ($BaCl_2$)	66
CPM M4	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1180°C in salt ($BaCl_2$+MgF_2) 3×2h at 560°C ($BaCl_2$)	65

Table 4.3: Continued

TSP 8 Cr18	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1120°C in salt ($BaCl_2$+MgF_2) 3×2h at 640°C ($BaCl_2$)	49
Micro-Melt M4	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1180°C in salt ($BaCl_2$+MgF_2) 3×2h at 560°C ($BaCl_2$)	64
Micro-Melt 23	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1170°C in salt ($BaCl_2$+MgF_2) 3×2h at 560°C ($BaCl_2$)	62
Micro-Melt 30	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1180°C in salt ($BaCl_2$+MgF_2) 3×2h at 560°C ($BaCl_2$)	66
Micro-Melt A 11 LVC	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1150°C in salt ($BaCl_2$+MgF_2) 3×2h at 540°C ($BaCl_2$)	58
Micro-Melt A 11	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1150°C in salt ($BaCl_2$+MgF_2) 3×2h at 540°C ($BaCl_2$)	63
T 15 Spray formed	1st preheating temperature 2nd preheating temperature Austenitizing temperature Tempering temperature\time	400°C in air 860°C in salt ($BaCl_2$) 1220°C in salt ($BaCl_2$+MgF_2) 3×2h at 540°C ($BaCl_2$)	67

4.3. Hardness measurement

Rockwell bulk hardness measurements were performed on polished surfaces at a 150 kg load using Rockwell hardness tester supplied by Otto Wolpert-Werke GMBH, Ludwigshafen, Germany. The observed hardness values are averages of eight readings taken at random locations throughout the sample. All the measured hardness values are tabulated along with heat treatment parameters in table 4.3.

4.4. Density measurement

Density measurements on conventional and powder metallurgical HIPed tool steels were carried out in annealed and hardened conditions at IWK. First, the test piece is weighed in the condition in which it was received. Then, test sample is put on an immersion basket suspended from a piece of thin wire and the mass of the test sample in water is determined. The weighing in air and water is shown in Figure 4.5 [18]. Ensure that all air bubbles are removed from the surface of the test samples and the supporting device before weighing in water. During the present investigation, the test samples are put inside soap water before measuring in water. The density values are calculated by using the following formulae.

$$\text{Density } \rho = \frac{m_L}{(m_L - m_W)} \cdot \rho_{Fl} \ [g/cm^3]$$

ρ_{Fl} - density of water [≈ 1 g/cm^3]

m_L - mass of the sample in air [g]

m_W - mass of the sample in water [g]

The observed values of densities are the average of three time measurements. The density of the test liquid (here water) also depends upon the test temperature. However, here the density of water is taken as an approximate value equal to 1 g/cm^3. The exact value of water density depending upon the temperature is given in reference [18] as a table.

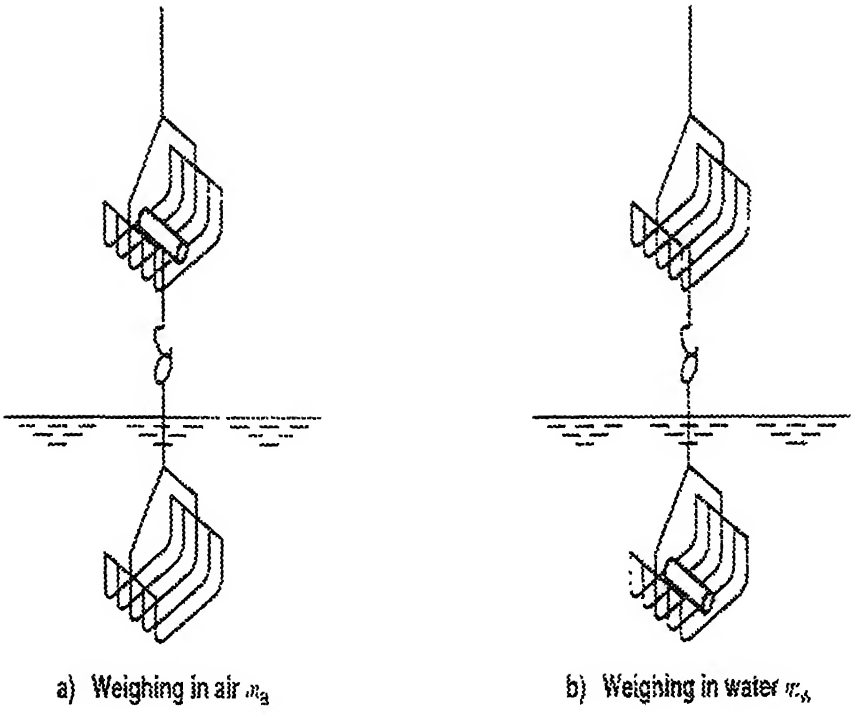

Figure 4.5: Weighing the samples in air and water [18].

4.5. Elastic properties measurements

Elastic properties at ambient temperatures or below are often determined by ultrasonic methods. Ultrasound techniques use the interaction of high-frequency sound waves with matter, in order to generate information about the physico-chemical properties. Such measurements have been established in numerous areas, like medicine, oceanography or material sciences [19-21]. In present study elastic properties of conventional and powder metallurgical tool steels were measured through ultrasonic transmission method at room temperature in annealed and heat-treated conditions.

4.5.1 Introduction

Ultrasound means acoustic signals in the frequency range from 10 kHz up to approx. 30 MHz. When such a sound wave propagates in a material it forces particles to oscillate. They oscillate around their equilibrium positions with a frequency equal to that of the ultrasonic wave. The movement can be parallel to the direction of propagation, so that the sound wave generates a compressional wave or longitudinal wave. If the movement is perpendicular to the direction of propagation, a shear wave or transversal wave is generated [20]. Figure. 4.6 shows the schematic representation of the propagation of an ultrasonic wave through material.

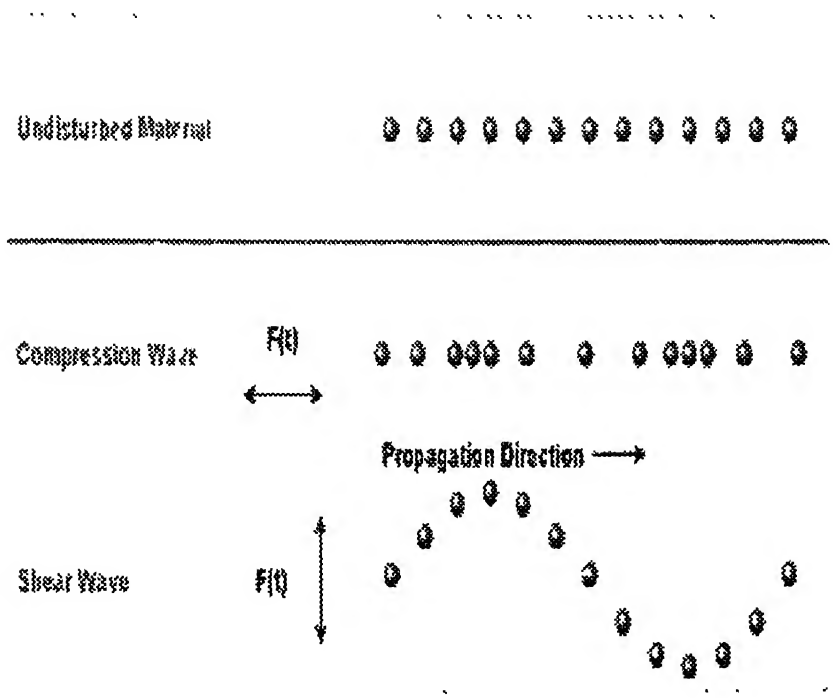

Figure. 4.6: Schematic representation of the propagation of an ultrasonic wave through a material. F (t) is a high frequency, sinusoidal force acting parallel or perpendicular to the surface of a sample [20].

4.5.2. Longitudinal and transversal ultrasonic waves

The first velocity usually determined is the longitudinal, often referred to as compressional, nondistortional, L wave, P wave, waves of dilatation, and irrotational waves. The longitudinal velocity is specimen-geometry to wavelength dependent.

The shear wave appears to be the most easily propagated waveform in nature and usually has the highest amplitude. Shear waves are often called transverse waves, distortional waves, rotational waves, torsional waves, and S waves. They are usually the most difficult kind of wave to generate with transducers, and since the shear velocity is approximately one-half the velocity of longitudinal waves, the shear wavelength is on the order of one-half the wavelength of longitudinal waves for the same frequency. For this reason it is frequently necessary to use a shear wave frequency that is one-half the maximum longitudinal wave frequency [19-20].

The simplest and most widely used technique to measure ultrasonic velocity is the so-called ultrasonic transmission technique. Figure 4.7 shows an instrument used for ultrasonic velocity measurement based on transmission method. All the measurements were carried out at IWK. The ultrasonic velocity measurements were performed on ultrasonic tester USIP 12 supplied by Krautkrämer GMBH &Co., Germany. The transducers for longitudinal and transversal velocity measurement are of 1 and 5 MHZ frequency respectively. Glycerine and honey were chosen as the couplants between specimen and transducer, depending on difference in viscosity and resonance requirements for the longitudinal transducer or the transversal transducer.

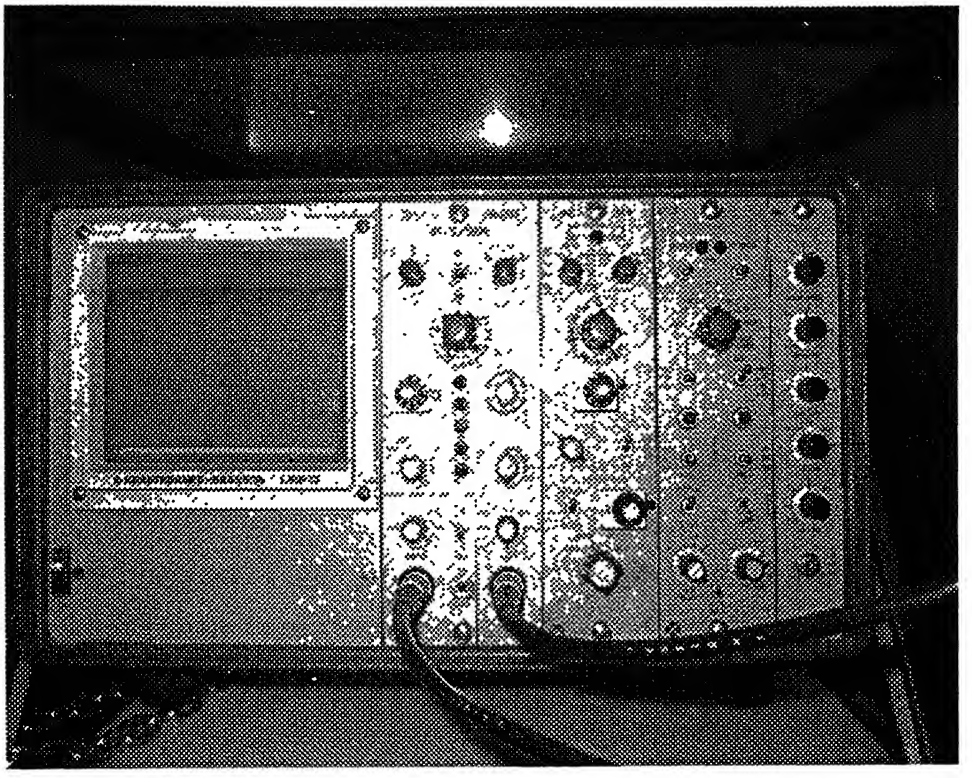

Figure 4.7: Instrument for ultrasonic velocity measurement based on transmission method.

4.5.3 Factors affecting performance and accuracy (ultrasonic equipment).

For an accurate ultrasonic velocity measurement there are certain factors, which need to be taken in account before starting measurements. All these factors are listed below. This section also includes the brief idea about coupling materials.

Factors affecting the performance and accuracy (Ultrasonic equipment)

1. Surface roughness of test piece: The best measurement accuracy is obtained when both the front and back surfaces of the test piece are smooth and parallel. If the contact surface is rough, the minimum thickness that can be measured will be increased because of sound reverberating in the increased thickness of the coupling layer. There will also be potential inaccuracy caused by variations in the thickness of the coupling layer beneath the transducer. Additionally, if either surface of the test piece is rough, the returning echo may be distorted due to the multiplicity of slightly sound paths seen by the transducer, and measurement inaccuracies will result.

2. Coupling technique: In direct contact transducer measurements, the coupling layer thickness is a part of the measurement and is compensated by a portion of the zero offset. If maximum accuracy is to be achieved, the coupling technique must be consistent. This is accomplished by using a coupling of reasonably low viscosity, employing only enough coupling to achieve reading, and applying the transducer with uniform pressure. A little practice will show the degree of moderate to firm pressure that produces repeatable readings. In general, smaller diameter transducers require less coupling force to squeeze out the excess coupling than large diameter transducers.

3. Taper or eccentricity: If the contact surface and back surface of the test piece are tapered or eccentric with respect to each other, the return echo will be distorted due to variation in sound path across the width of the beam. Accuracy of measurement will be reduced. In severe cases no measurement will be possible.

4. Calibration: The accuracy of any ultrasonic measurement is only as good as the accuracy and care with which the gage has been calibrated. All quality ultrasonic

gages provide a method for calibrating for the sound velocity and zero offset appropriate for the application at hand. It is essential that this calibration be performed and periodically checked in accordance with the manufacturer's instructions. Sound velocity must always be set with respect to the material being measured. Zero offset is usually related to the type of transducer, transducer cable length and mode of measurement being used.

Selection of coupling material (Ultrasonic equipment)

Coupling material: A wide variety of coupling materials may be used in ultrasonic gauging. We have found that glycerine is suitable for longitudinal wave transmission, while, in difficult applications (shear wave transmission) where maximum transfer of sound energy is required, honey is recommended. Other suitable couplings for measurements at normal temperatures may include greases, gels, various oils and silicone fluids.

4.5.4 Measurement procedure

The longitudinal and transversal velocities were calculated by following procedure.

1. Measure the dimension of the specimen blocks (d) in the directions through which you will send the ultrasound (smallest dimension).
2. Connect the longitudinal wave transducer (marked CLF5) to the pulse receiver and then turn on the oscilloscope.
3. Set the pulse receiver to: pulse height "Low", Mode switch "UP" (for a single transducer), Damping-1, Pulser at A; Gains dB=0. Note that it may be necessary to adjust these values for different specimens and transducers.
4. Hold the transducer against the test specimen using a small amount of the glycerine couplant. Adjust the oscilloscope settings until you see a train of echoes, similar to that shown in Figure 4.8.
5. Make a precise measurement of velocity (c) by keeping the distance between the first and the second echo corresponds to maximum measured length (d_s) at the setting.

6. Then, calculate transversal velocity (c_s) by the following formula.

$$c_s = c \times \frac{d}{d_s} \qquad 4.1$$

Where

d: Actual sample length

c: Echo velocity corresponds to maximum measured sample length.

d_s Maximum measured sample length at screen of ultrasonic apparatus

c_s: Echo velocity in sample

7. Repeat the longitudinal measurements at least three times on each specimen and then take the average value.
8. Replace the longitudinal wave transducer with the shear wave transducer.
9. Set the pulser receiver to: pulse height "Hi", mode switch "DOWN" (dual), Pulser at G, Damping-7, Gain dB=0. Note that it may be necessary to adjust these values for different specimens and transducers.
10. Hold the shear wave transducer against the specimens using shear wave couplant (honey). Because it is difficult to transmit shear waves across an interface, it is necessary to use firm pressure between the transducer and the specimen. But do not exceed the pressure that you can apply by hand- do not clamp transducer as this will result in damage to the device.
11. Again measure velocity (c_s) by above-mentioned method and put in formulae 4.1 to get the desired value of transversal velocity.
12. Repeat the shear wave measurement at least three times and take the average value.
13. When finished, clean off the transducers and specimen blocks using a damp paper towel.

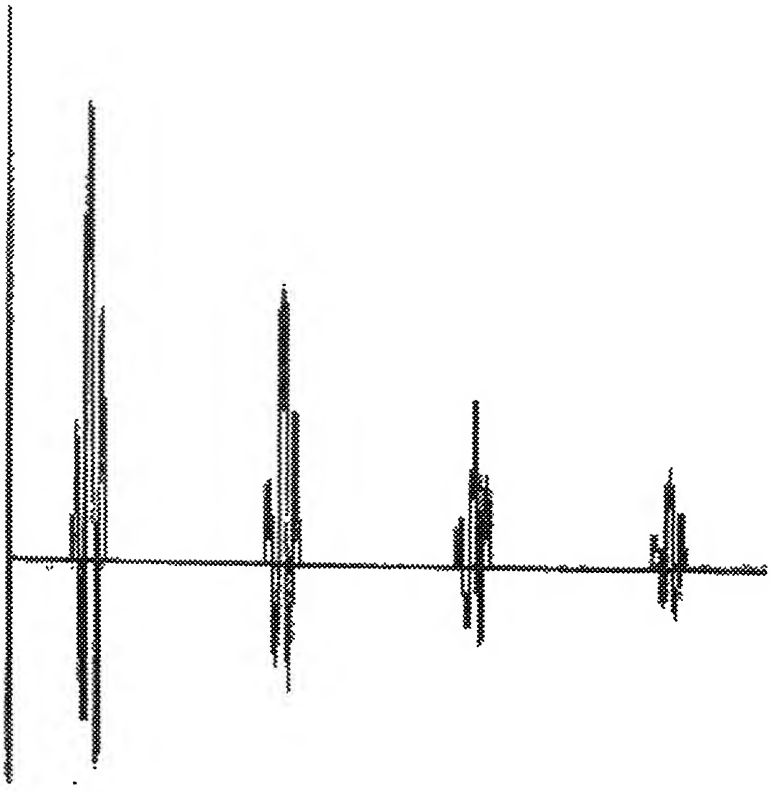

Figure 4.8: Schematic of echoes received from repeated round trips through a specimen [19].

4.5.5 Calculation of elastic properties

After the measurements of densities and ultrasonic velocities in both annealed and heat treated conditions, following mathematical relations were used in order to calculate the elastic properties such as E, G, υ.

$$G = c_{trans}^2 \cdot \rho \qquad 4.2$$

$$E = \left(\frac{3 - 4\left(\frac{c_{trans}}{c_{long}}\right)^2}{1 - \left(\frac{c_{trans}}{c_{long}}\right)^2} \right) \cdot G \qquad 4.3$$

$$\upsilon = \frac{E}{2 \cdot G} - 1 \qquad 4.4$$

Where

E: Elastic modulus

G: Shear modulus

υ: Poisson's ratio

c_{trans}: Transversal velocity

c_{long}: Longitudinal velocity

ρ: Density

Thus, by the measurements of ρ, C_{trans} and C_{long}, calculate E, G and υ.

4.6. Heat capacity measurements

One of the fundamental concepts of modern science and the basis of thermodynamics is the connection between heat and energy. An entire class of materials analysis techniques is based on the ability to transfer heat to a material and monitor the effects. This class of techniques is known as thermal analysis. Differential Scanning Calorimetry (DSC) is a convenient and highly accurate method for performing thermal analysis on a wide variety of materials. In present study DSC technique was used for the determination of heat capacity of selected tool steels. Specific heat capacity measurements were carried out up to 800°C in argon atmosphere on each sample. All the experiments were performed on NETZSCH 404C DSC apparatus at IKKM.

4.6.1 Measuring principle

The differential scanning calorimeter consists of a test chamber, with a furnace, a temperature and a differential sensor as well as a means to sustain a test chamber environment of inert purge gas. The schematic view of DSC equipment is shown in Figure 4.9 and the detail of the sample holder in Figure 4.10. Differential Scanning Calorimetry (DSC) is based upon the detection of changes in the heat content of a sample with temperature. As thermal energy is supplied to the sample, its enthalpy increases and its temperature rises by an amount determined by the specific heat of the sample, for a given energy input. Samples of the test substance and a reference material are subjected to the same controlled temperature programme. The temperatures of the two samples are compared, and the electrical power supplied to each heater is adjusted so that the temperatures of both the sample and the reference remain equal to the programmed temperature. The signal, corresponding to the energy absorption rate by the sample, is proportional to the specific heat of the material [22].

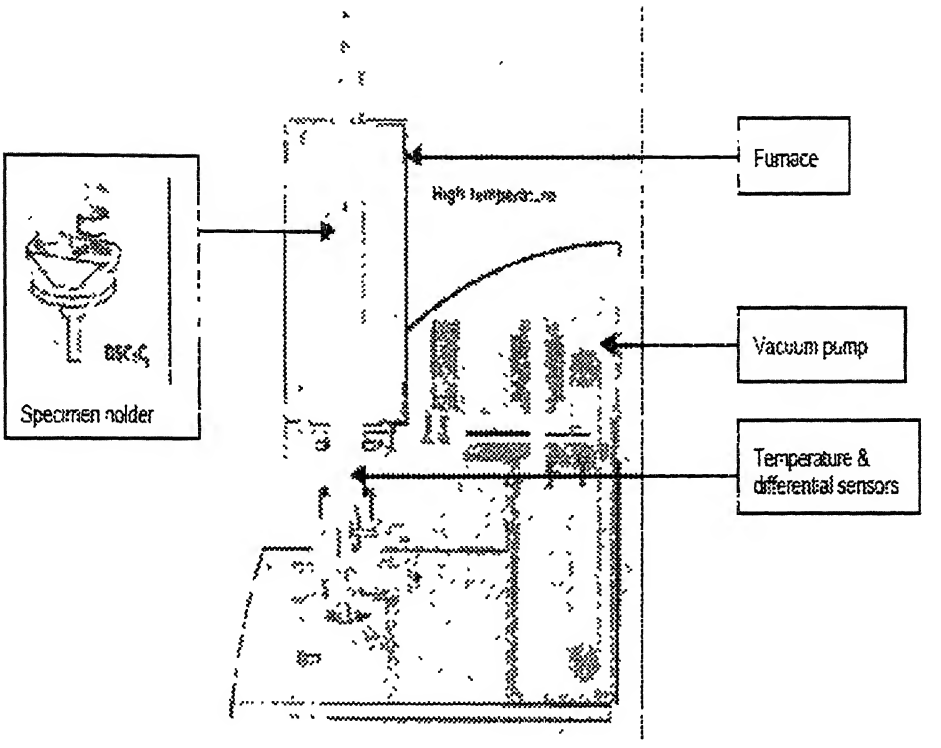

Figure 4.9: Schematic view of DSC equipment [22].

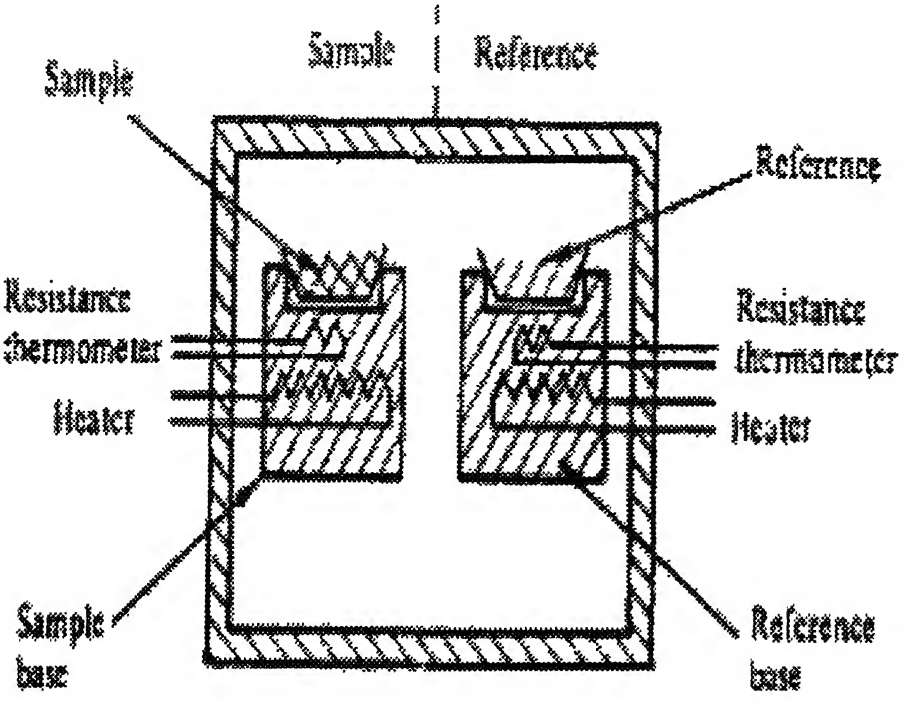

Figure 4.10: DSC sample holder [22].

4.6.2 Sample preparations

Samples to be used in differential scanning calorimetry are small pieces that are enclosed in special pans. The appropriate mass range for samples is 1 mg to 10 mg. The specimens used for specific heat testing are cylindrical plates, of diameter 5 ± 0.1mm and of height 1 ± 0.2mm, with at least one side flat.

Figure 4.11 shows the drawing of sample used in present investigation. All the samples for specific heat measurements were prepared at mechanical workshop of IWK.

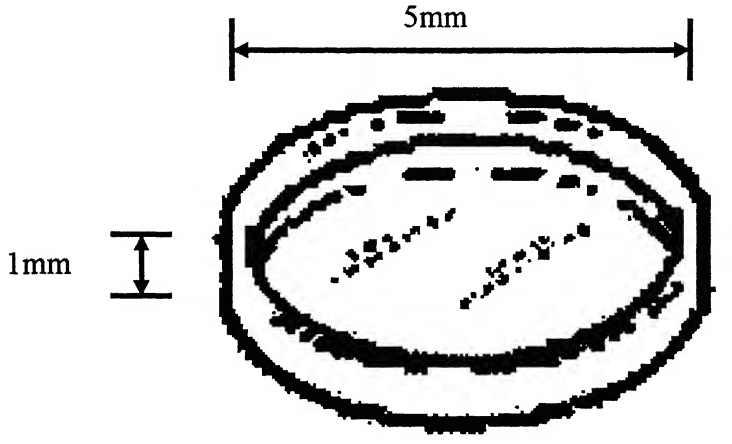

Figure 4.11: Specimen drawing for specific heat measurement.

4.6.3 Basic components, technical features and specimen environment

The experiments were performed using a NETZSCH 404C DSC instrument (Figure 4.12) with the following components:

1) Measuring unit: including the high temperature SiC oven, sample and reference holders, and vacuum and/or inert gas connections
2) Specimen crucibles: Corundum Al_2O_3
(T_{max}: 1650°C, 0.085 cm^3).
3) Thermocouple: Type S (Pt10%Rh-Pt).
4) NETZSCH TASC/414 T-controller
5) Furnace power supply
6) Computer system running the data acquisition and analysis software (WindowsNT).

Technical features:

Sample environment: The measurements were usually accomplished in argon atmosphere. A measurement in helium or vacuum is likewise possible, conditionally with a substantially smaller sensitivity of the equipment.

Reference material: Sapphire (NIST)

Temperature range: [30°C (RT) to 1650°C]
The accessible temperature range depends also on the thermocouples used, namely:

Type E: (-120° to 700°C), Chromel-Constantan.
Type K: (RT to 800°C), Chromel-Alumel.
Type S: (RT to 1650°C), Pt10%Rh-Pt.
Type B: (150° to 1650°C), Pt30%Rh-Pt6%Rh.

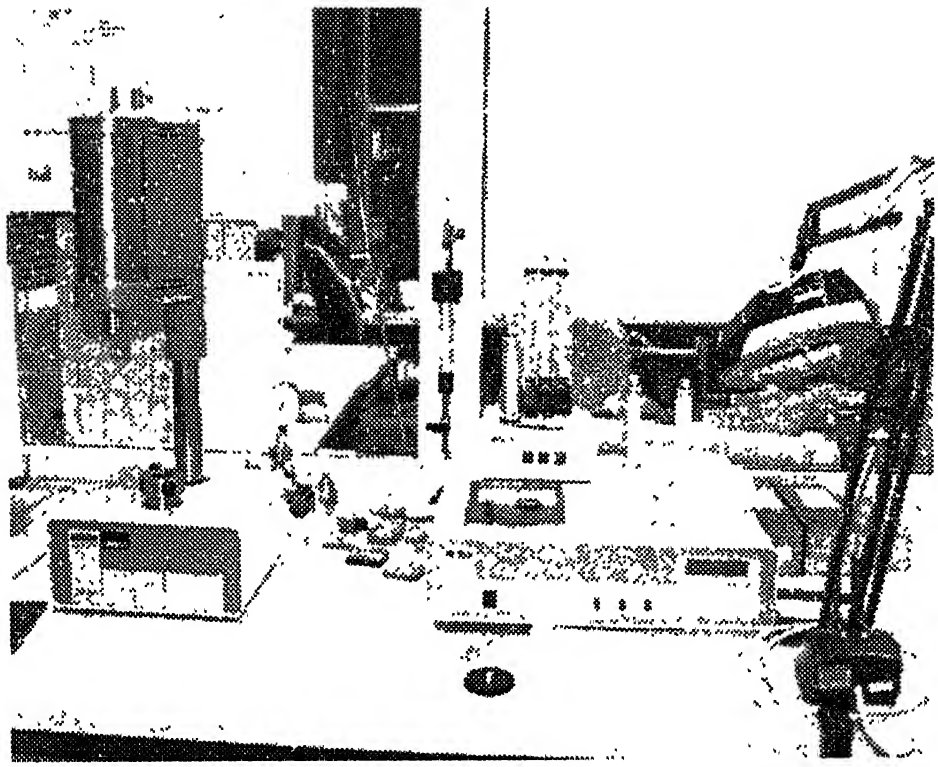

Figure 4.12: Typical experimental set up for specific heat measurement using differential scanning calorimetry.

4.6.4 Factors affecting the performance and accuracy (DSC)

Following factors should be taken in account during measurements of specific heat with DSC.

1 Samples should be properly cleaned before starting DSC experiment. Cleaning can be done in ethanol or in some other suitable chemical reagent as per sample chemistry.
2 Size of samples is very small in DSC. So accurate measurement of weight of sample is very important. Slight difference may cause error in measurements.
3 Do not touch the crucible with bare hands. Use tweezers to handle crucibles.
4 Before placing the pans in the DSC, insure that the bottoms are flat so that they make good thermal contact with the heaters.

Samples should be planning parallel and the face in contact with the crucible must be polished to have the optimal heat transmission.

4.6.5 Operational Procedure

The operating procedure of specific heat measurements is divided into three phases.

Phase 1: Baseline

Weigh a clean, empty specimen holder plus lid to a precision of ±0.01mg.The mass of the crucible plays an important role for the quality of the results. Purge the DSC apparatus with argon at a flow rate of 50mL/min throughout the experiment. The temperature profile is then applied to the two empty crucibles. Heat or cool the DSC test chamber to the initial temperature. For high temperature measurements, the initial temperature is generally 40°C. Hold isothermally the DSC test chamber at the initial temperature for duration sufficient to reach equilibrium that is around 10 minutes. Heat the test specimen from the initial to the final temperature (a rate of 20°C/min is usual). Finally, cool the DSC chamber to ambient temperature at a slower rate (10°C/min).

Phase 2: Measurement of the reference material

Weigh the sapphire sample and the specimen holder plus lid to a precision of ±0.01mg. The reference material, usually sapphire, is carefully placed into the first crucible and the results are recorded. Prior to the testing, the sample shall be cleaned, for instance by ultrasonic and ethanol. It is very important that the specimen is mounted properly. Otherwise, an artefact will be observed on the DSC curve. Purge the DSC apparatus with argon. Heat or cool the DSC test chamber to the initial temperature and hold isothermally the DSC test chamber at the initial temperature for duration sufficient to reach equilibrium. Heat the test specimen from the initial to the final temperature at the same rate used for the baseline measurement. Finally, cool the DSC chamber to ambient temperature at a slower rate.

Phase 3: Measurement of the unknown material

Weigh the tool steel sample and the specimen holder plus lid to a precision of ±0.01mg. The specimen is carefully placed into the second crucible and the results are recorded. Prior to the testing, the sample shall be cleaned, for instance by ultrasonic and ethanol. Purge the DSC apparatus with argon at a flow rate of 50mL/min throughout the experiment. Heat or cool the DSC test chamber to the initial temperature and hold isothermally the DSC test chamber at the initial temperature for duration sufficient to reach equilibrium. Heat the test specimen from the initial to the final temperature at the same rate used for the baseline measurement (a rate of 20°C/min is usual). Finally, cool the DSC chamber to ambient temperature at a slower rate.

For getting precise results in specific heat measurement; there are few factors which demand carefulness during measurements. All these factors are listed in appendix F.

4.6.6 Calculation of specific heat

The results are obtained in the form of DSC potential versus time curves, with a corresponding temperature profile. The calculations are based on following principle.

The results obtained from the sapphire can be written as function of temperature and using the baseline results:

$$m_{Sapphire} \cdot C_P^{Sapphire} \cdot T = DSC^{Sapphire}(T) - DSC^{baseline}(T) \qquad 4.5$$

The results obtained from the unknown material can be written as function of temperature and using the baseline results:

$$m_{material} \cdot C_P^{material} \cdot T = DSC^{material}(T) - DSC^{baseline}(T) \qquad 4.6$$

Equating the two equations gives the specific heat of the unknown material:

$$C_p^{material} = \frac{DSC^{material}(T) - DSC^{baseline}(T)}{DSC^{sapphire}(T) - DSC^{baseline}(T)} \cdot \frac{m_{sapphire}}{m_{material}} \cdot C_p^{sapphire} \qquad 4.7$$

All the above-mentioned calculations are done in software automatically without any manual calculation.

4.7 Statistical analysis

भारतीय प्रौद्योगिकी संस्थान कानपुर
अवाप्ति क्र० A 148423

A multilinear regression analysis [23] was performed to correlate the data of calculated physical properties with chemical composition(C, V, W, Cr, Mo, Co). The multilinear regression analysis assumes that physical properties (ρ, E, G, ν and C_p) correlate linearly with the chosen chemical elements. We analysed the relationships between the physical property and each of the variables, and we observed a linear dependence of physical property on every one of the parameters.

This result demonstrates that the linear behaviour is not merely an artefact of the large number of data points. The statistical analysis was performed using Mehr regression function with origin 7G software. In order to check the quality of a least squares fitting to the original data, we analysed the coefficient of correlation for each regression performed.

For the final analysis, six parameters are considered. Nevertheless, the data set of thirty seven tool steels is large enough to take into account six parameters.

4.7.1 Factors affecting the precision of correlation approach

Following are the factors that affect the precision of correlation approach.

1. All the chemical compositions are not measured, therefore the nominal chemistry were used. This is clearly a source of scatter.
2. All the steels had been hot worked and, thus, an alignment of structural constituents had taken place. Particularly in conventional high speed steels a very high anisotropy develops and the ultrasound measurements lose their validity since they are strictly based on isotropic material behaviour.

Chapter 5

RESULTS AND DISCUSSIONS

I have divided the presentation of the results into several sub-chapters. First, density measurements, relationship between density change and hardness, followed by elastic property measurements, and finally, specific heat measurements.

5.1 Density measurements

Results of density measurements in annealed and heat treated condition are given in appendix A. The final density value for each sample is based on averages of three measurements. In order to correlate density with chemistry of tool steels, a multiple linear regression analysis is used. Figure 5.1 correlates the density data of conventional and powder metallurgical tool steels in annealed state with chemical composition. Similarly, Figure 5.2 correlates the density values in heat-treated state with chemical composition. The values of coefficient of correlation for both the plots are tabulated in table 5.1. The final equations obtained after regression analysis is as follows.

In annealed state

$$\rho = 7.8192 - 0.0045(\%Cr) + 0.0204(\%Mo) - 0.0366(\%V) + 0.0495(\%W) + 0.0019(\%Co) - 0.0566(\%C) + 0.0028(\%CV)\ [g/cm^3] \quad 5.1$$

In hardened and tempered state

$$\rho = 7.8010 - 0.0033(\%Cr) + 0.0213(\%Mo) - 0.0359(\%V) + 0.0491(\%W) + 0.0019(\%Co) - 0.0719(\%C) + 0.0032(\%CV)\ [g/cm^3] \quad 5.2$$

From above equation, it is quite evident that in both cases (annealed and hardened), tungsten and molybdenum adds to density, vanadium, chromium and

carbon reduce the density, statistically cobalt and the product of C and V (%CV) has little influence.

Equation 5.1 and 5.2 helps in procuring the density of other chemically known tool steels in annealed and heat treated state.

The average drop in density values from annealed state to heat treated state is about 0.015-0.035g/cm^3, less for lower hardness hot working tool steels, more for highest hardness high speed steels. This drop in density value from annealed state to heat treated state is expected. In heat treat process, formation of martensite from austenite results in unavoidable volume expansion of nearly 0.4%. This increase in volume results in decrease in density at the same mass. The exact percentage of volume expansion depends upon alloying content, austenitizing temperature, time and quenching process.

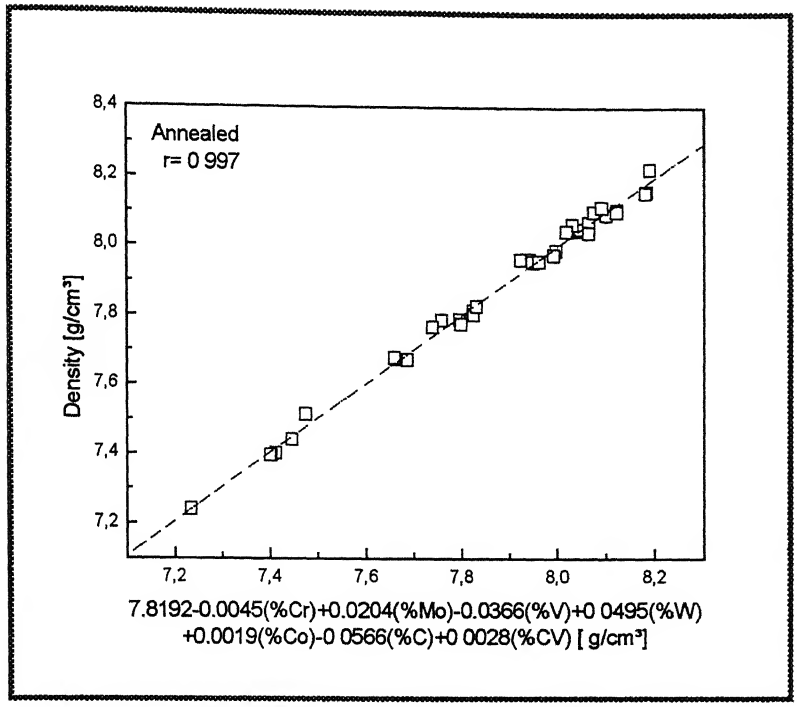

Figure 5.1: Effect of chemical composition of conventional and powder metallurgical hot work, cold work and high speed tool steels on room temperature density in annealed state.

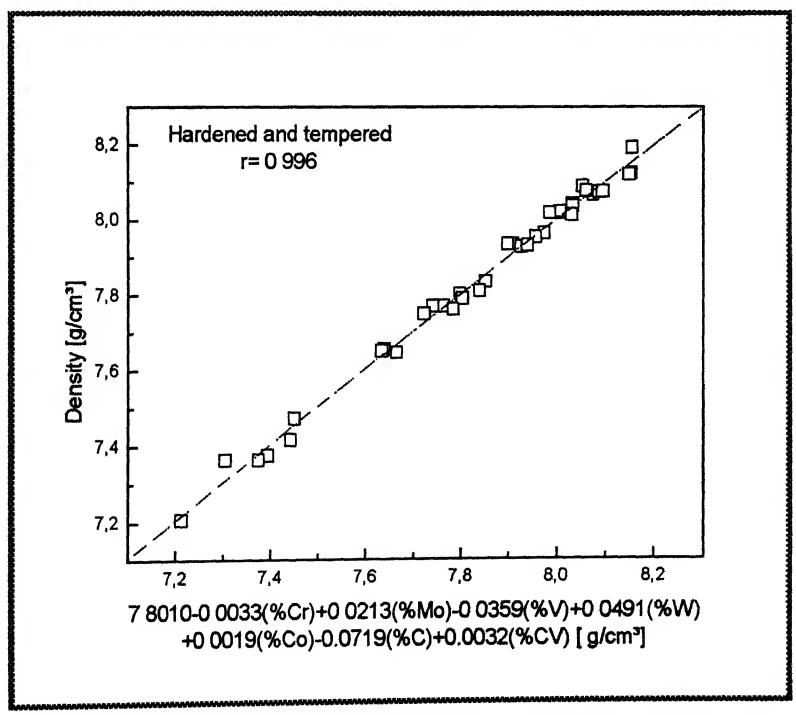

Figure 5.2: Effect of chemical composition of conventional and powder metallurgical hot work, cold work, high speed tool steels on room temperature density in hardened and tempered state.

Table 5.1: Coefficient of correlation for density plots

Condition	Coefficient of correlation
Annealed	0.997
Hardened and tempered	0.996

5.2 Relationship between density change ($\Delta\rho$) and hardness (HRC)

Hardness measurements were done in order to see the relationship between hardness and density change from annealed to heat treated state on conventional and powder metallurgical tool steels. Table 5.2 presents the results of hardness measurements together with density change from annealed to heat treated state. Figure 5.3 shows the relationship between hardness and density change. The relationship between hardness (HRC) and density change ($\Delta\rho$) is linear. This trend was expected. Higher change in density corresponds to higher hardness and vice versa. Tool steels attributed with higher change in density means higher volume expansion after heat treatment, this volume expansion being due to entrapping carbon in the BCC lattice. With more carbon in martensite the density change and the bulk hardness will increase.

Table 5.2: Results of hardness and density measurement.

Tool steel grade	Type	Density in annealed state [g/cm³]	Density in hardened and tempered state [g/cm³]	Change in density ($\Delta\rho$)	Hardness HRC
1.2343	Conventional	7.759	7.743	0.016	47
1.2344	Conventional	7 739	7.724	0.015	50
1.2367	Conventional	7.825	7.800	0.025	53
101≈2343	Conventional	7.826	7.805	0.021	46
TSP8 Cr18	PM HIPed	7.412	7.395	0.017	49
CPM 3V	PM HIPed	7.665	7.640	0.025	59
CPM 10V	PM HIPed	7.404	7.376	0.028	63
CPM 15V	PM HIPed	7.235	7.212	0.023	63
CPM Re X M4	PM HIPed	7.945	7.910	0.035	65
CPM M4	PM HIPed	7.924	7.899	0.025	65
CPM T15	PM HIPed	8.185	8.155	0.030	67
1.3343	PM HIPed	8.102	8.076	0.026	65
1.3344	PM HIPed	8.042	8.009	0.033	66
TSP 23	PM HIPed	8.046	8.008	0.038	61
TSP 8	PM HIPed	7.475	7.452	0.023	60
TSP 5	PM HIPed	8.124	8.087	0.037	66
TSP 4	PM HIPed	7.949	7.927	0.022	60
ESP 4	Spray formed	7.998	7.975	0.023	58

Table 5.2: Continued

TSP 1	PM HIPed	7 796	7.766	0.030	67
TSP 30	PM HIPed	8.066	8.034	0.032	66
1.3247	PM HIPed	7.993	7.957	0.036	67
1.3243	PM HIPed	8.123	8.096	0.027	65
T15-HIP	PM HIPed	8.191	8.156	0.035	62
1.2888	Conventional	8.076	8.054	0.022	49
1.2889	Conventional	7 799	7.785	0.014	45
1.2379	Conventional	7.686	7.666	0.020	58
ESP 32	Spray formed	8.092	8.061	0.031	65
1.2365	Conventional	7.832	7.821	0.011	52
Micro-Melt M4	PM HIPed	7.963	7.940	0.023	64
Micro-Melt 23	PM HIPed	8.020	7.987	0.033	62
Micro-Melt 30	PM HIPed	8.066	8.032	0.034	66
Micro-Melt A 11LVC	PM HIPed	7.466	7.444	0.022	58
Micro-Melt A 11	PM HIPed	7.401	7.386	0.015	63
ESP 23	Spray formed	7.660	7.635	0.025	58
T 15 Spray formed	Spray formed	8.182	8.150	0.032	67
1.2999	Conventional	7.868	7.853	0.015	53

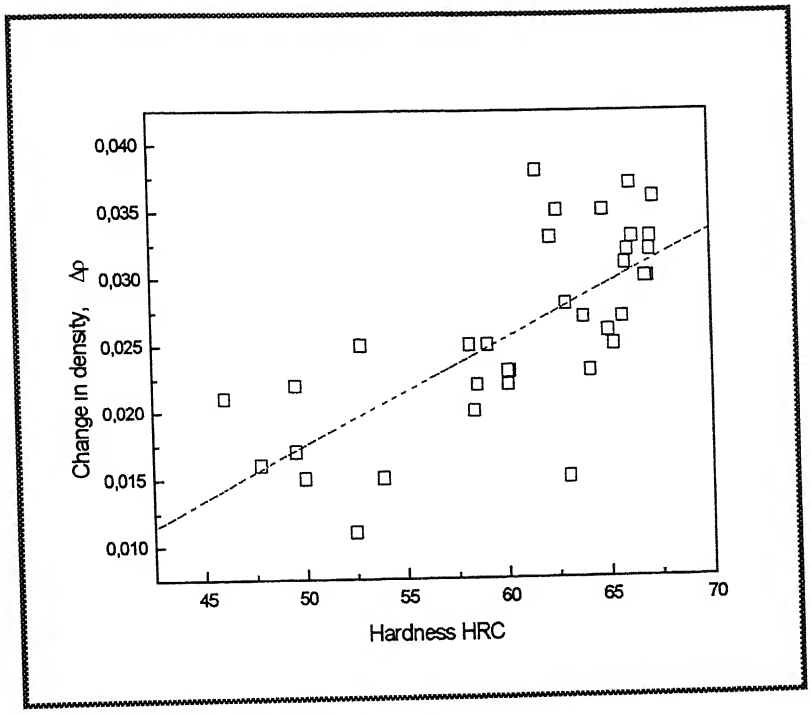

Figure 5.3: The relationship between changes in density ($\Delta\rho$) from annealed to hardened state in conventional and powder metallurgical tool steel and hardness (HRC).

5.3 Elastic properties measurements

Data of shear velocity and longitudinal velocity measurements for conventional and powder metallurgical tool steel samples in annealed and heat treated state are given in appendix A. Final velocity values are based on averages of three times measurements in annealed and heat treated state. Calculated elastic properties (E, G and ν) based on velocity measurements and density (by equation 4.2, 4.3 and 4.4) are also given in appendix A. Again, final values of elastic properties (E, G and ν) are based on averages of three times calculations.

A multiple linear regression analysis is used in order to correlate chemistry of tool steels with elastic properties. For correlation purpose, all the major alloying elements (C, V, W, Mo, Cr, Co) are taken in account. Figure 5.4, 5.5 correlates Young's modulus data with chemical composition in annealed and heat treated state respectively. Similarly, Figure 5.6, 5.7 and 5.8, 5.9 correlate shear modulus and Poisson ratio respectively in annealed and heat treated state. The values of coefficient of correlation for each plot are tabulated in table 5.3.

Results of regression analysis give an approximation for the calculations of elastic properties of other tool steels in annealed and heat treated condition separately. Equation 5.3, 5.4 and 5.5 give E modulus, G modulus and ν Poisson's ratio respectively in annealed state. While, equations 5.6, 5.7 and 5.8 give E modulus, G modulus and Poisson's ratio in hardened and tempered state. Now, with these equations we can find the elastic properties of other chemically known tool steels in annealed and heat treated state separately.

Table 5.3: Coefficient of correlation for E, G and ν plots

Condition	Coefficient of correlation		
	E modulus plot	G modulus plot	ν Poisson's ratio
Annealed	0.941	0.930	0.775
Hardened and tempered	0.961	0.957	0.891

In annealed condition

$$E = 173.903 + 1.798(\%Cr) + 1.950(\%Mo) + 4.84(\%V) + 2.190(\%W) + 0.347(\%Co) + 7.145(\%C) - 1.046(\%CV)\ [10^3 N/mm^2] \quad 5.3$$

$$G = 65.068 + 0.769(\%Cr) + 0.918(\%Mo) + 2.077(\%V) + 0.952(\%W) + 0.187(\%Co) + 3.059(\%C) - 0.418(\%CV)\ [10^3 N/mm^2] \quad 5.4$$

$$\nu = 0.3298 - 0.0016(\%Cr) - 0.0026(\%Mo) - 0.0052(\%V) - 0.0014(\%W) - 0.0008(\%Co) - 0.0023(\%C) + 0.0007(\%CV) \quad 5.5$$

In hardened and tempered condition

$$E = 164.604 + 2.248(\%Cr) + 2.30(\%Mo) + 6\,213(\%V) + 1.953(\%W) + 0.457(\%Co) + 4.155(\%C) - 1.161(\%CV)\ [10^3 N/mm^2] \quad 5.6$$

$$G = 61.112 + 1.011(\%Cr) + 1.020(\%Mo) + 2.866(\%V) + 0.884(\%W) + 0.239(\%Co) + 1.402(\%C) - 0.508(\%Co)\ [10^3 N/mm^2] \quad 5.7$$

$$\nu = 0.3351 - 0.0018(\%Cr) - 0.0020(\%Mo) - 0.0081(\%V) - 0.0016(\%W) - 0.0011(\%Co) - 0.0012(\%C) + 0.0014(\%CV) \quad 5.8$$

In both annealed and heat treated state, chromium, molybdenum, tungsten, vanadium and carbon add to elastic modulus and shear modulus. But, the effect of vanadium and carbon is much more prominent in enhancing the elastic modulus and shear modulus compared to other alloying elements. Cobalt is least effective among all alloying elements. Combined effect of carbon and vanadium i.e. effect of %CV is negative in both the cases.

If we look at the results of elastic properties measurements, an important thing is to observe that annealed state having higher value of elastic properties compared to same tool steel in hardened and tempered state. Comparison is given in table 5.4. This trend was expected. As we know from atomic theory, dependence of elastic property on binding energy and equilibrium interatomic spacing (Eq. 5.9).

$$E = \left.\frac{d\sigma}{d\varepsilon}\right|_{\varepsilon=0} = \left.\frac{d\frac{F}{r_0^2}}{d\frac{r-r_0}{r_0}}\right|_{r_0} = \left.\frac{1}{r_0}\frac{dF}{dr}\right|_{r_0} = \frac{S_0}{r_0} = \left.\frac{1}{r_0}\frac{dU^2}{dr^2}\right|_{r_0} = \frac{nm}{r_0^3}U_b \qquad 5.9$$

Where r_0 = equilibrium interatomic spacing

U_b = binding energy

Note: *Derivation of this relation is given in appendix C.*

From this relation, we can conclude that materials having lower bonding energy and higher interatomic spacing have lower elastic properties. During heat treatment, austenite (FCC) transforms to martensite (BCT). This transformation results in atomic rearrangement causing volume expansion. The exact value of this expansion varies from steel to steel. This expansion causes an increase in equilibrium interatomic spacing and thereby reduction of elastic modulus.

In order to cross check the result of elastic properties measurement, separate measurements were done at Saarbrücken, Germany. All the measurements were carried out at Institut Zerstörungsfreie Prüfverfahren (IZFP). Appendix D present the comparison of results obtained at two places. Majority of samples were successfully measured at IZFP. The results are in agreeable range, with the difference of 1-2% in shear modulus and 3-4% in Young's modulus compared to IWK results. Few samples were not showing any signal at IZFP while, few of them (marked *) showed surprising results compared with IWK results. This difference may be due to unplane surface of sample. There may be other possible reasons for this difference. There is plenty of room for research in this area; further investigations and study may help to draw some plausible conclusions.

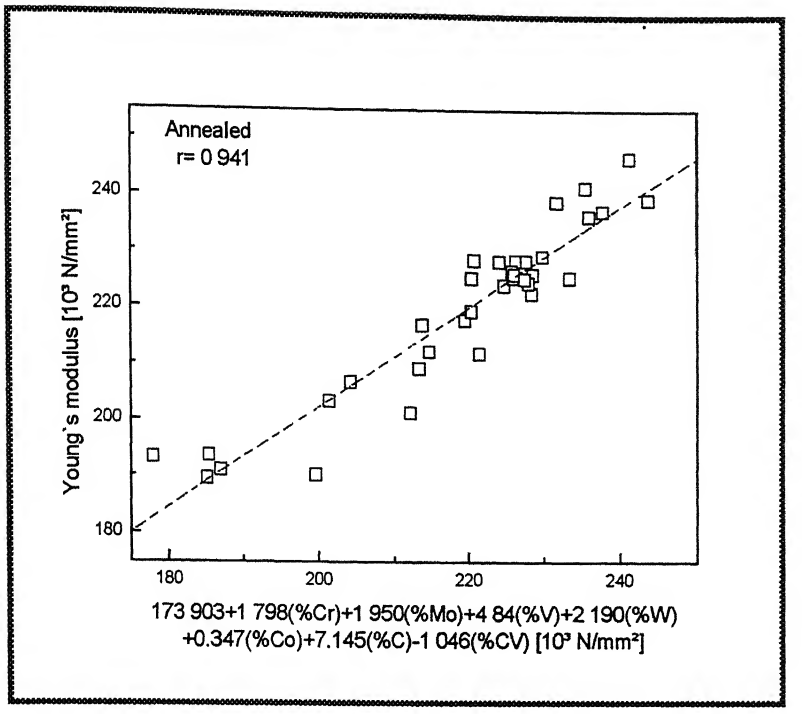

Figure.5.4: Effect of alloying elements in conventional and powder metallurgical HIP tool steels on Young's modulus in annealed condition.

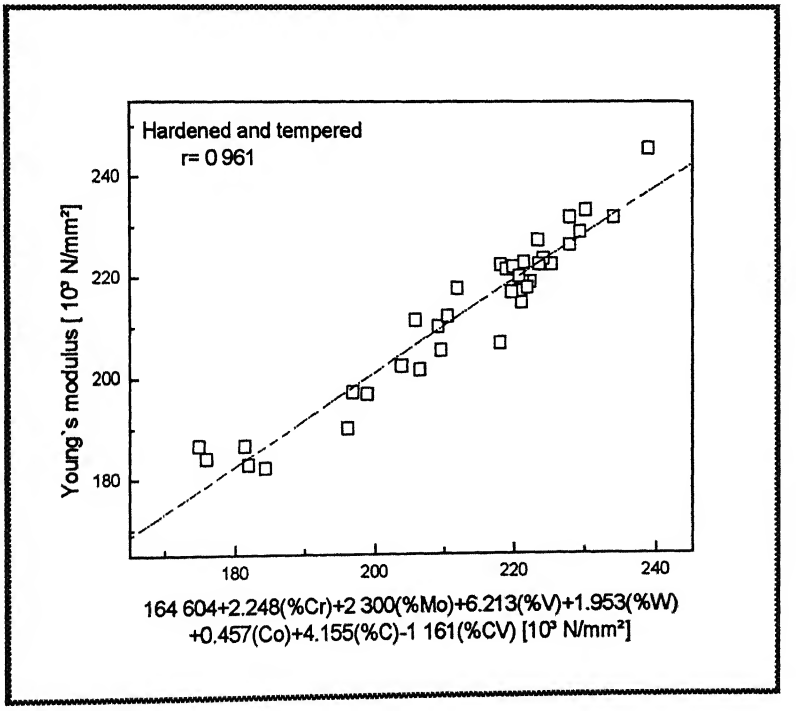

Figure 5.5: Effect of alloying elements in conventional and powder metallurgical HIP tool steels on Young's modulus in hardened and tempered condition.

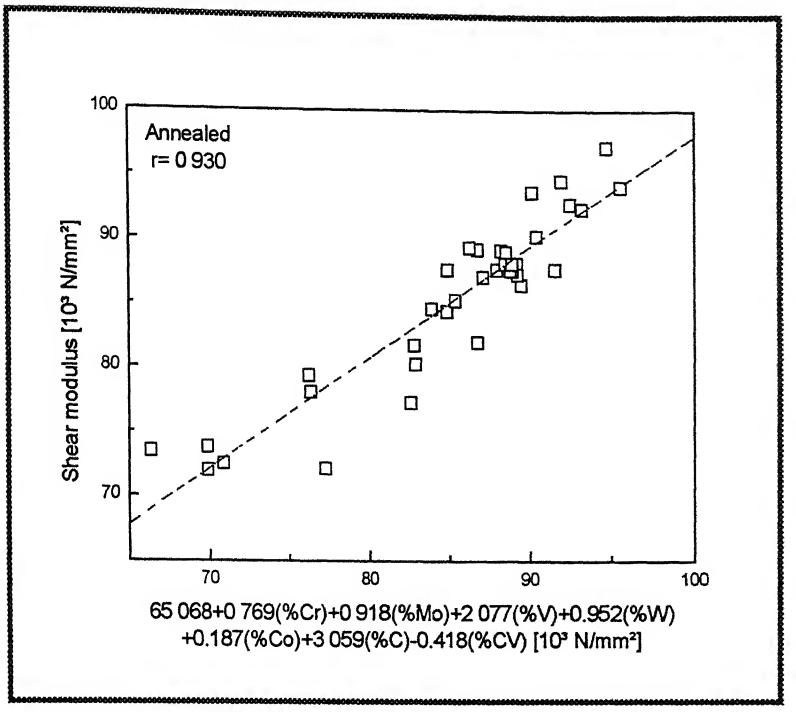

Figure 5.6: Effect of alloying elements in conventional and powder metallurgical HIP tool steels on shear modulus in annealed condition.

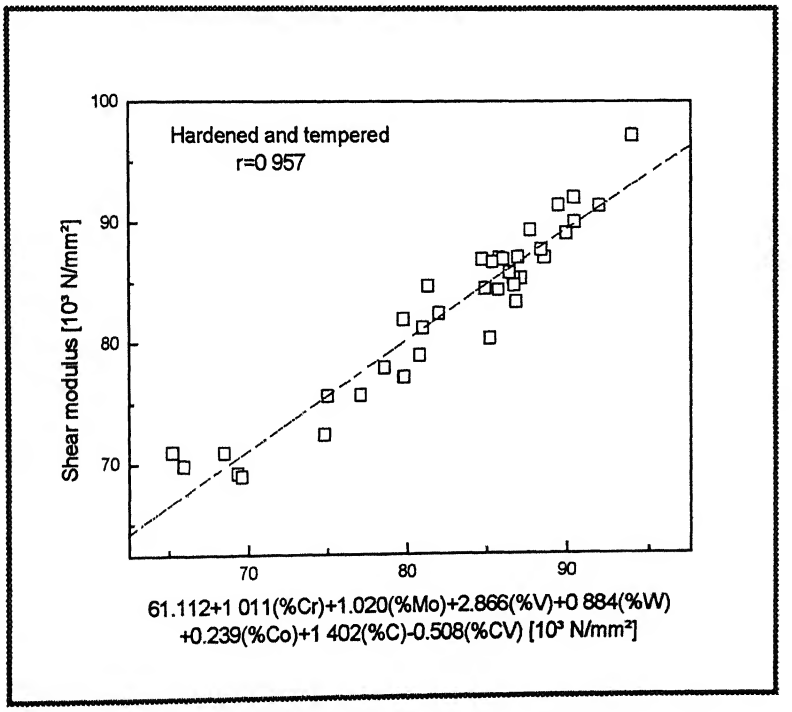

Figure 5.7: Effect of alloying elements in conventional and powder metallurgical HIP tool steels on shear modulus in hardened and tempered condition.

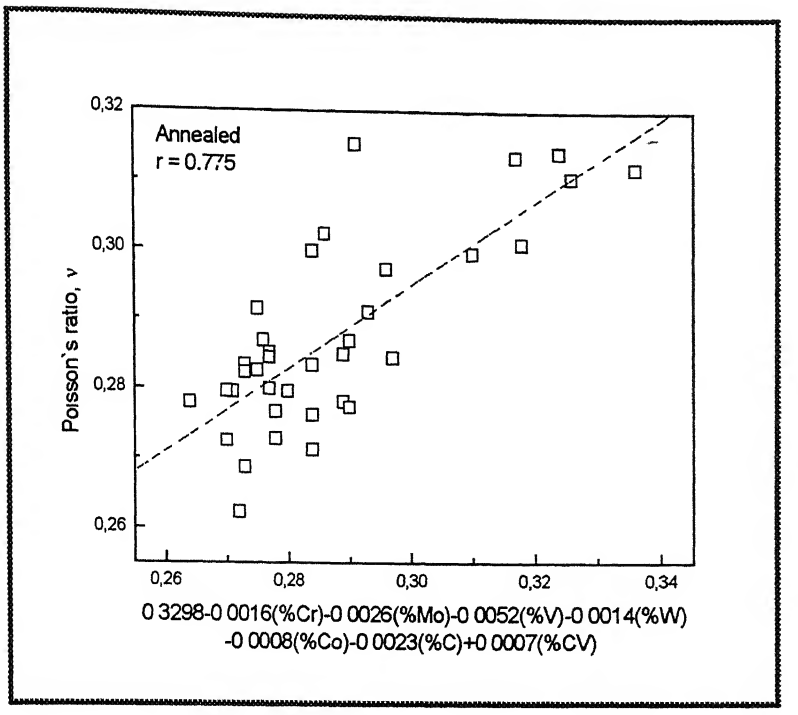

Figure 5.8: Effect of alloying elements in conventional and powder metallurgical HIP tool steels on Poisson's ratio in annealed condition.

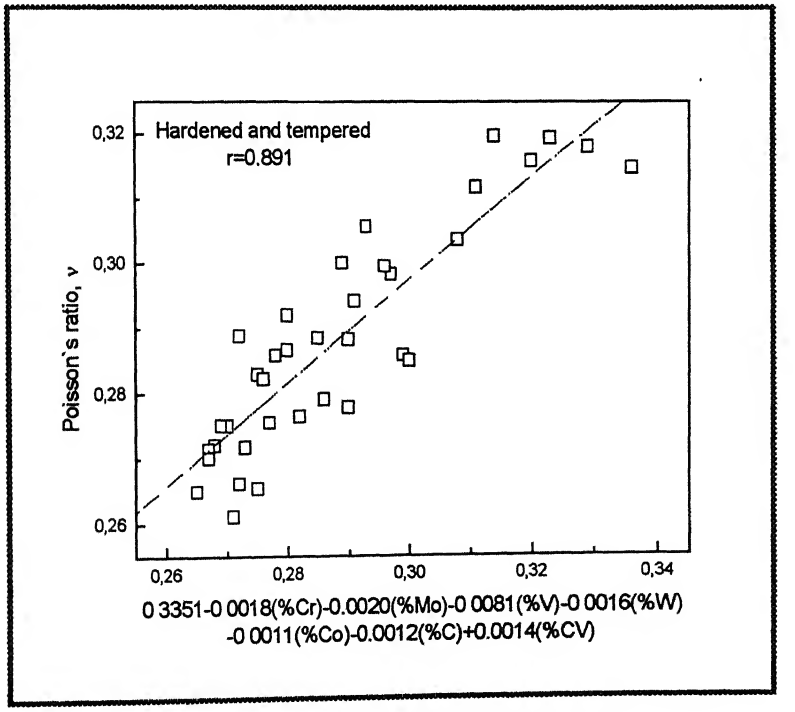

Figure 5.9: Effect of alloying elements in conventional and powder metallurgical HIP tool steels on Poisson's ratio in hardened and tempered condition.

Table 5.4: Comparison of elastic properties in annealed and heat treated condition

Steel grade	E-modulus (GPa)		G-modulus (GPa)		ν-Poisson's ratio	
	Annealed	Hardened and tempered	Annealed	Hardened and tempered	Annealed	Hardened and tempered
1.2343	199.64	182.09	77.28	69.38	0.291	0.314
1.2344	177.61	174.45	66.35	65.25	0.336	0.336
1.2367	185.42	181.42	69.86	68.52	0.326	0.323
101≈2343	186.93	175.43	70.90	65.94	0.317	0.329
TSP 8 Cr18	241.34	238.53	94.78	93.72	0.272	0.271
CPM 3V	204.31	203.96	76.25	78.56	0.310	0.297
CPM 10V	228.60	225.36	89.25	88.64	0.280	0.270
CPM 15V	229.94	227.63	90 46	89.69	0.270	0.268
CPM ReX M4	233.46	222.41	91.62	87.18	0.273	0.275
CPM M4	226.36	221.30	88.08	86.71	0.284	0.275
CPM T15	236.04	223.50	93.29	87.74	0.264	0.273
1.3343	219.54	209.21	84.85	80.98	0.293	0.291
1.3344	228.47	221.16	89.50	86.87	0.276	0.272
TSP 23	220.44	211.39	84.88	81.32	0.297	0.299
TSP 8	227.66	221.51	88.26	85.81	0.289	0.290
TSP 5	231.82	228.26	90.20	89.50	0.284	0.275
TSP 4	224.82	220.92	87.12	84.93	0.289	0.300

Table 5.4: Continued

ESP 4	226.31	218.21	88.58	84.76	0.277	0.286
TSP1	201.45	196.48	76.38	74.95	0.318	0.308
TSP 30	224.12	218.98	86.78	85.38	0.290	0.282
1.3247	213.86	205.92	83.91	79.79	0.273	0.290
1.3243	220.42	210.53	85.38	81.86	0.290	0.285
ASP 30	220.76	219.96	86.30	86.08	0.278	0.277
T 15 HIP	235.58	230.23	92.04	90.44	0.278	0.272
1.2888	221.44	218.13	86.79	85.24	0.275	0.279
1.2889	212.28	198 82	82.59	77.08	0.284	0.289
1.2379	213.41	206.59	82.89	79.82	0.286	0.293
ESP 32	243.81	234.12	95.65	92.46	0.273	0.265
1.2365	185.25	184.39	69.93	69.63	0.324	0.323
Micro-Melt M4	225.81	220.79	88.48	86.47	0.275	0.276
Micro-Melt 23	227.69	219.75	89.11	85.76	0.277	0.280
Micro-Melt 30	228.15	222.00	89.25	86.77	0.277	0.278
Micro-Melt A 11LVC	224.40	224.22	87.97	88.43	0.275	0.267
Micro-Melt A 11	226.106	223.68	88.93	88.08	0.270	0.269
T 15 spray formed	237.86	229.47	92.55	90.48	0.284	0.267
ESP 23	214.72	209.56	82.82	80.80	0.296	0.296

5.4 Specific heat measurements

Results of specific heat measurement on selected conventional and powder metallurgical tool steels in annealed and heat treated state are given in appendix E. All the measurements were carried in argon atmosphere upto 800°C. Plots of C_P vs. temperature for each sample in annealed and heat treated state are also given in appendix B. In annealed state, all the plots are approaching towards single peak upto 800°C; which corresponds to magnetic transition. While, plots of hardened and tempered state show three peaks at various temperatures. The first peak corresponds to the formation of ε carbide ($Fe_{24}C$), second peak indicates martensitic decomposition and third peak is of magnetic transition.

Figure 5.10 and 5.11 shows the DSC diagram of all the selected tool steels in annealed and heat treated state respectively Table 5.5 presents the specific heat of selected tool steels in annealed and heat treated state at 400°C. The value of heat capacity of tool steels in annealed condition seems to be very plausible. All the selected steels are in same agreeable range. While, in hardened and tempered state its magnitude is highly anomalous. The reason for this anomaly is not clear completely. For better understanding about variation in specific heat of tool steels in hardened and tempered state, investigations on larger number of samples is required then only we can come to any conclusion

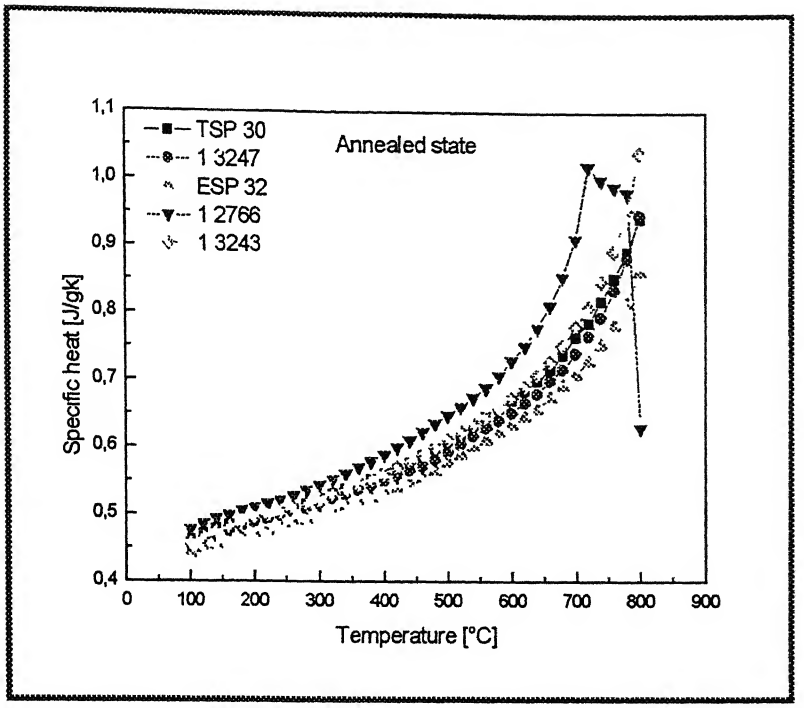

Figure 5.10: Variation in heat capacity of selected tool steels with temperature in annealed condition.

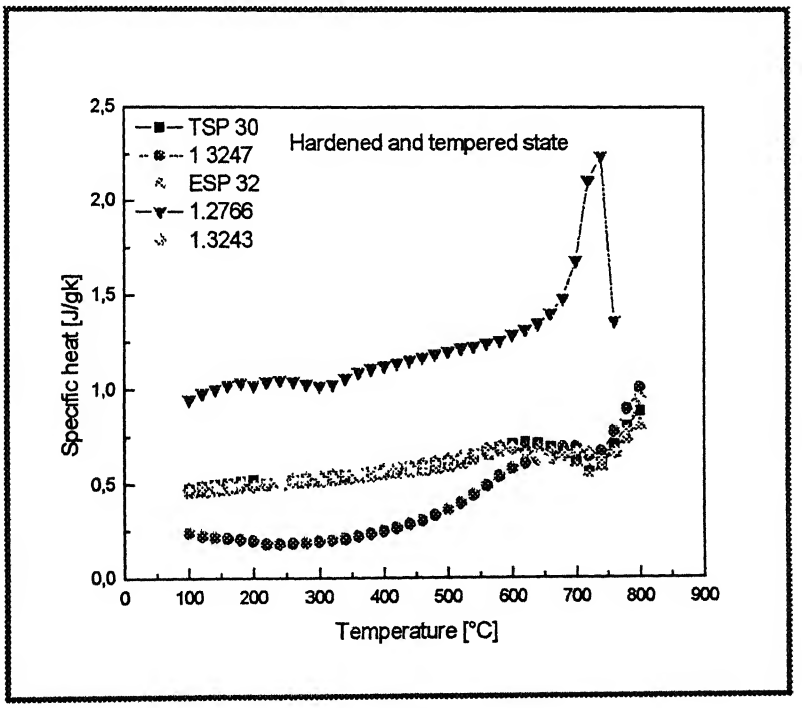

Figure 5.11: Variation in heat capacity of selected tool steels with temperature in hardened and tempered.

Table 5.5: Comparison of specific heat values in annealed and hardened and tempered state at 400°C of selected samples.

Sample designation	Specific heat in annealed state [J/gk]	Specific heat in hardened and tempered state [J/gk]
1.2766	0.588	1.111
1.3243	0.560	0.572
1.3247	0.549	0.246
TSP 30	0.560	0.571
ESP 32	0.529	0.546

In order to see the effect of chemical composition on specific heat of tool steel a multilinear regression analysis is used. For correlation purpose, tungsten, molybdenum, carbon and vanadium were selected as variables. Figure 5.12 shows the effect of chemical composition on true specific heat of selected tool steels in annealed condition at 400°C. Similarly, Figure 5.13 presents the effect of chemistry on true specific heat of selected tool steels in hardened and tempered state. The values of coefficient of correlation for both the plots are tabulated in table 5.6.

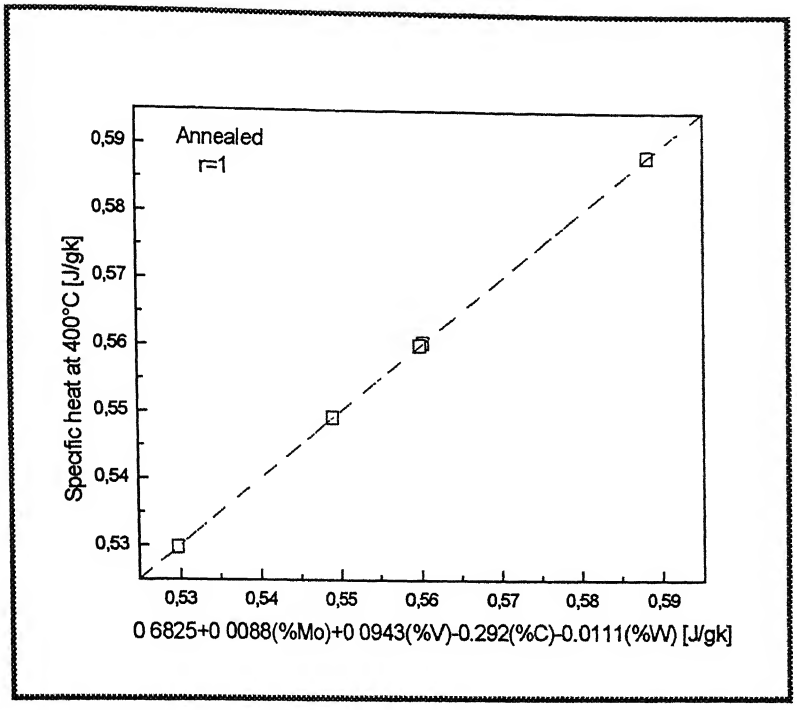

Figure 5.12: Effect of chemical composition on true specific heat of conventional and HIP tool steels in annealed state.

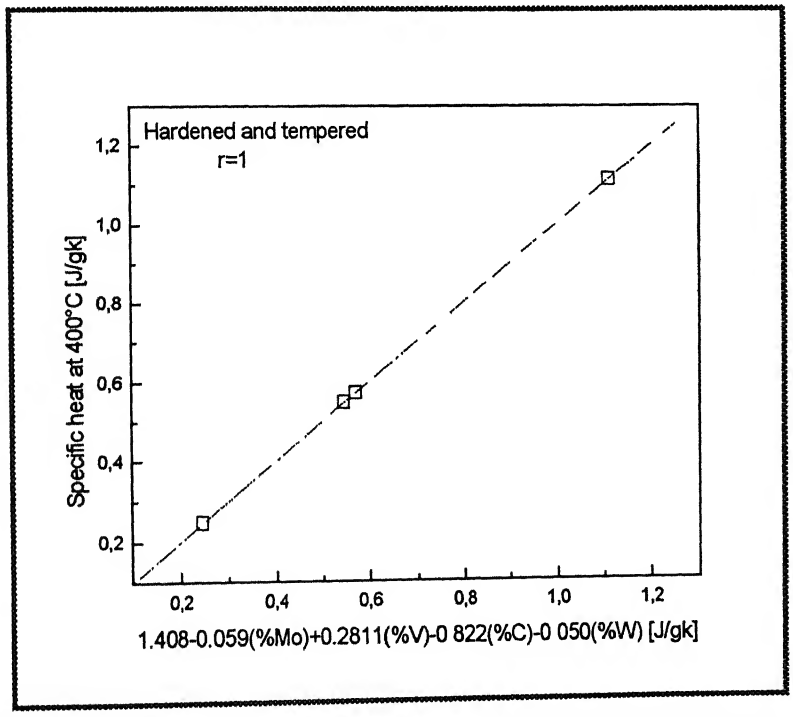

Figure 5.13: Effect of chemical composition on true specific heat of conventional and HIP tool steels in hardened and tempered state.

Table 5.6: Coefficient of correlation for specific heat plots.

Condition	Coefficient of correlation
Annealed	1.0
Hardened and tempered	1.0

The final equations obtained after multilinear regression analysis is as follows:

In annealed state:

$$C_P = 0.6825 + 0.0088(\%Mo) + 0.0943(\%V) - 0.292(\%C) - 0.0111(\%W)\ [J/gk] \quad 5.10$$

In hardened and tempered state:

$$C_P = 1.408 - 0.059(\%Mo) + 0.2811(\%V) - 0.822(\%C) - 0\ 050(\%W)\ [J/gk] \quad 5.11$$

From the results of regression analysis it is quite clear that the dependence of heat capacity of tool steels on alloying chemistry is much more pronounced in hardened and tempered state compared to annealed state. Among various selected alloying elements the effect of vanadium and carbon is very significant compared to other alloying elements. Carbon decreases the heat capacity while, vanadium increases the heat capacity in annealed and heat treated state. The effect of other alloying elements (molybdenum and tungsten) is not significant.

Equation 5.10 and 5.11 helps in procuring the heat capacity of other chemically known tool steels in annealed and heat treated state.

Chapter 6

CONCLUSIONS

Present work has led to better understanding of physical properties of tool steels with respect to their chemistry. Role of each alloying element of tool steel on its physical properties is clarified. The following conclusions were obtained from this study of correlationship between physical property and chemistry of tool steels in annealed and heat treated state.

1. In annealed and heat treated tool steels, tungsten and molybdenum addition increases the density, while chromium, vanadium and carbon reduce the density.
2. The average drop in density values from annealed state to heat treated state is about 0.015-0.035g/cm^3, less for lower hardness hot working tool steels, more for highest hardness high speed steels.
3. The relationship between density drop ($\Delta\rho$) from annealed to heat treated state and hardness (HRC) is linear. Hardness value increases with increase in density drop and vice versa.
4. For the first time, the present study sheds some light on the shear modulus and Poisson's ration of high alloy tool steels. These properties have so far not been reported in the accessible literature. This work is the first study which distinguishes systematically physical properties in the annealed state from those in the hardened and tempered condition.
5. Results of multilinear regression analysis show a strong dependence of elastic properties on chemistry of tool steels in annealed and heat treated state.
6. All the major alloying elements (C, V, W, Cr, Mo, Co) of tool steels help in enhancing the elastic properties in annealed and heat treated state. The effect of vanadium and carbon as alloying elements is much more prominent in enhancing the elastic properties of tool steels, compared to other alloying elements.
7. Compared to annealed state, tool steels in hardened and tempered state have slightly lower elastic modulus and shear modulus.

8. Dependence of heat capacity of tool steels on alloying chemistry is much more in hardened and tempered condition compared to annealed condition.
9. The influence of vanadium and carbon is significant in altering the heat capacity of tool steels compared to other alloying elements in annealed and hardened and tempered state. Vanadium helps in enhancing, while carbon reduces the heat capacity of tool steels.
10. Table 6.1 summarizes the final equations obtained. With these equations we can estimate the physical properties (density, elastic properties and heat capacities) of other chemically known tool steels in annealed and heat treated state separately.

Table 6.1: Equations obtained in annealed and heat treated state.

Property	Condition	Equations obtained
Density (ρ)	Annealed	7.8192-0.0045(%Cr)+ 0.0204(%Mo) - 0.0366(%V) +0.0495(%W)+0.0019(%Co)-0.0566(%C) + 0.0028(%CV) [g/cm^3]
	Hardened and tempered	7.8010-0.0033(%Cr)+ 0.0213(%Mo) - 0.0359(%V) +0.0491(%W)+0.0019(%Co)-0.0719(%C) + 0.0032(%CV) [g/cm^3]
Elastic modulus (E)	Annealed	173.903 + 1.798(%Cr) + 1.950(%Mo) + 4.84(%V) +2.190(%W)+0.347(%Co)+7.145(%C) - 1.046(%CV) [10^{3}N/mm^2]
	Hardened and tempered	164.604 + 2.248(%Cr) + 2.30(%Mo) + 6.213(%V) +1.953(%W)+0.457(%Co)+4.155(%C) - 1.161(%CV) [10^{3}N/mm^2]
Shear modulus (G)	Annealed	65.068 + 0.769(%Cr) + 0.918(%Mo) + 2.077(%V) + 0.952(%W) + 0.187(%Co)+3.059(%C) - 0.418(%CV) [10^{3}N/mm^2]
	Hardened and tempered	61.112 + 1.011(%Cr) + 1.020(%Mo) + 2.866(%V) + 0.884(%W) + 0.239(%Co) + 1.402(%C) - 0.508(%Co) [10^{3}N/mm^2]

Poisson's ratio (ν)	Annealed	0.3298-0.0016(%Cr) - 0.0026(%Mo) - 0.0052(%V) - 0.0014(%W) - 0.0008(%Co) - 0.0023(%C) + 0.0007(%CV)
	Hardened and tempered	0.3351 - 0.0018(%Cr)-0.0020(%Mo) - 0.0081(%V) - 0.0016(%W) - 0.0011(%Co) - 0.0012(%C) + 0.0014(%CV)
Specific heat (C_P)	Annealed	0.6825 + 0.0088(%Mo) + 0.0943(%V) - 0.292(%C)- 0.0111(%W) [J/gk]
	Hardened and tempered	1.408 - 0.059(%Mo) + 0.2811(%V) - 0.822(%C) - 0.050(%W) [J/gk]

Chapter 7

FUTURE WORK

During this research, one interesting thing came about the variations in the magnitude of specific heat of tool steels in hardened and tempered condition. Data of specific heat of tool steels in hardened and tempered condition is highly anomalous. Further investigations on large number of conventional and powder metallurgical tool steels will help to draw some conclusions about variation in magnitude of specific heat of tool steels. There should be some proper reason behind variations in magnitude of heat capacity of tool steels in hardened and tempered condition.

Further research will be needed to investigate thermal conductivity and thermal diffusivity of tool steels. At present there is no proper correlation between these properties and chemistry of tool steels. There should be some proper correlationships between alloying elements and these properties in annealed and heat treated condition.

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Appendix: A

Table 1: Data of density and ultrasonic measurement in annealed condition.

Steel designation	ρ g/cm^3	S.D	C_T m/s	S.D	C_L m/s	S.D	G N/mm^2	E N/mm^2	ν
1.2343	7.759	0.001	3156	16.73	5820	28.28	77283	199642	0.291
1.2344	7.739	0.001	2928	28.28	5928	17.88	66357	177611	0.336
1.2367	7.825	0 001	2988	17.88	5896	16.73	69864	185424	0.326
1.2766	7.834	0.002	2996	16.73	5868	17.88	70319	186159	0.323
101≈2343	7.826	0.001	3010	10.00	5832	33.46	70904	186931	0.317
TSP 8 Cr 18	7.412	0.004	3576	16.73	6408	10.95	94784	241348	0.272
CPM 3V	7.665	0.002	3188	17.88	6088	10.95	76256	204318	0.310
CPM 10V	7.404	0.000	3472	10.95	6288	10.95	89256	228601	0.280
CPM 15V	7.235	0.003	3536	21.90	6308	10.95	90465	229941	0.270
CPM Re X M4	7.945	0.001	3396	21.90	6084	14.14	91623	233468	0.273
CPM M4	7.924	0.003	3334	16.73	6084	14.14	88083	226360	0.284
CPM T15	8.185	0.002	3376	8.94	5972	10.95	93294	236045	0.264
1.3343	8.102	0.001	3236	26.07	5988	10.95	84851	219541	0.293

Table 1: Continued

1.3344	8.042	0.002	3336	32.86	6004	8.94	89507	228470	0.276
TSP 23	8.046	0.002	3244	26.07	6052	10.95	84887	220444	0.297
TSP 8	7.475	0.001	3436	32.86	6316	8.94	88265	227666	0.289
TSP 5	8.124	0.002	3332	22.80	6080	20.00	90206	231826	0 284
TSP 4	7.949	0.001	3312	17.88	6092	10.95	87129	224820	0.289
ESP 4	7.998	0.002	3328	10.95	5996	8.94	88587	226316	0.277
TSP 1	7.796	0.001	3130	14.14	6068	16.43	76385	201452	0.318
TSP 30	8.066	0.002	3280	14.14	6044	32.86	86786	224124	0.290
1.3247	7.993	0.001	3240	15.81	5812	30.33	83914	213864	0.273
1.3243	8.123	0.001	3242	17.88	5970	10.00	85387	220425	0.290
ASP 30	8.032	0.000	3278	10.95	5916	8.94	86306	220760	0.278
T 15 HIP	8.191	0.002	3352	17.88	6062	4.47	92041	235582	0.278
1.2888	8.076	0.002	3278	31.93	5892	17.88	86793	221440	0.275
1.2889	7.799	0.002	3254	19.49	5940	24.28	82590	212282	0.284
1.2379	7.686	0.000	3284	16.73	6012	10.95	82894	213418	0.286
ESP 32	8.092	0.001	3438	17.88	6158	10.95	95652	243810	0.273

Table 1: Continued

1 2365	7.832	0.003	2988	10.95	5870	10.00	69932	185250	0.324
Micro Melt M4	7.963	0.003	3333	11.54	5993	11.54	88485	225818	0.275
Micro Melt 23	8.020	0.002	3333	11.54	6006	11.54	89118	227693	0.277
Micro Melt 30	8.066	0.002	3326	11.54	6006	11.54	89258	228150	0.277
Micro Melt A 11LVC	7.466	0.002	3433	17.32	6166	15.27	88833	226023	0.271
Micro Melt A11	7.401	0.001	3466	11.54	6186	11.54	88939	226106	0.270
T 15 Spray formed	8.182	0 000	3363	5.77	6135	0.000	92554	237864	0.284
ESP 23	7.660	0.002	3288	11.54	6112	17.88	82821	214724	0.296

Table 2: Data of density and ultrasonic measurement in hardened and tempered condition.

Steel designation	ρ g/cm^3	S.D	C_T m/s	S.D	C_L m/s	S.D	G N/mm^2	E N/mm^2	ν
1.2343	7.743	0.003	2993	23.09	5730	10.00	69383	182096	0.314
1.2344	7.724	0.003	2906	11 54	5846	11.54	65258	174455	0.336
1.2367	7.800	0.002	2964	16.73	5808	10.95	68526	181427	0.323`
101≈2343	7.805	0.000	2906	11.54	5773	11.54	65942	175433	0.329
TSP 8 Cr 18	7.395	0.008	3560	0.00	6366	11.54	93725	238539	0.271
CPM 3V	7.640	0.006	3206	11.54	5980	0.00	78560	203968	0.297
CPM 10V	7.376	0.008	3466	11.54	6186	11.54	88643	225362	0.270
CPM 15V	7.212	0.001	3526	11.54	6273	11.54	89698	227639	0.268
CPM Re X M4	7.910	0.006	3320	17.32	5980	20.00	87188	222410	0.275
CPM M4	7.899	0.021	3313	11.54	5956	5.77	86719	221304	0.275
CPM T15	8.155	0.004	3280	20.00	5876	15.27	87743	223507	0.273
1.3343	8.076	0.000	3166	23.09	5840	20.00	80989	209216	0.291

Table 2: Continued

1.3344	8.009	0.004	3293	11.54	5893	11.54	86873	221164	0.272
TSP 23	8.008	0.013	3186	11.54	5960	0.00	81320	211399	0.299
TSP 8	7.452	0.004	3393	11.54	6246	5.77	85815	221516	0.290
TSP 5	8.087	0.026	3326	30.55	5976	20.81	89507	228264	0.275
TSP 4	7.927	0.002	3273	11.54	6133	11.54	84939	220923	0.300
ESP 4	7.975	0.008	3260	0.00	5966	23.09	84761	218212	0.286
TSP 1	7.766	0.000	3106	11.54	5926	23.09	74956	196485	0.308
TSP 30	8.034	0.010	3260	10.00	5920	20.00	85385	218986	0.282
1.3247	7.957	0.001	3166	11.54	5826	11.54	79791	205924	0.290
1.3243	8.096	0.007	3180	0.00	5806	11.54	81869	210537	0.285
ASP 30	8.034	0.001	3273	11 54	5900	20.00	86082	219968	0.277
T 15 HIP	8.156	0.008	3330	10.00	5956	5.77	90448	230230	0.272
1.2888	8.054	0.005	3253	11.54	5880	0.00	85248	218131	0.279
1.2889	7.785	0.007	3146	11.54	5786	23.09	77083	198822	0.289
1.2379	7.666	0.007	3226	30.55	5973	11.54	79824	206599	0.293
ESP 32	8.061	0.000	3386	11.54	6000	20.00	92463	234124	0.265

Table 2: Continued

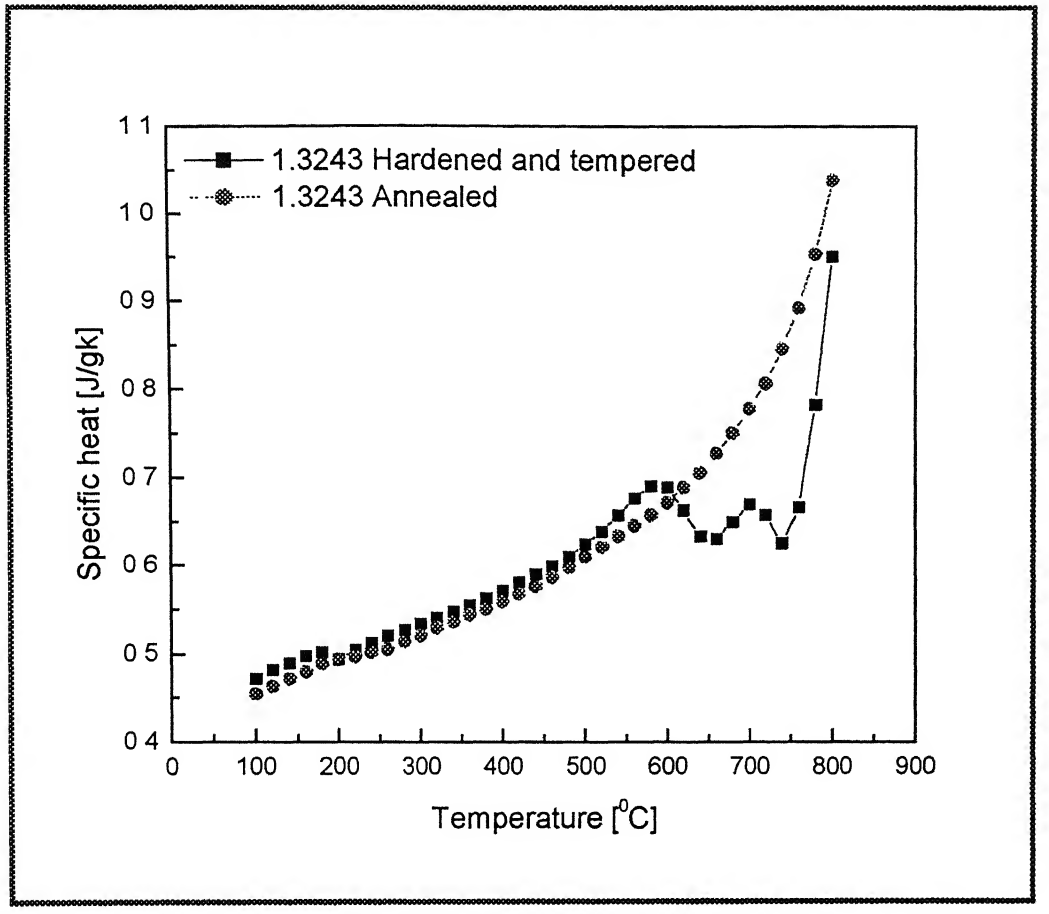
1.2365	7.821	0.002	2980	14.14	5844	45.60	69454	183947	0.323
Micro Melt M4	7.940	0.005	3300	20.00	5940	20.00	86471	220793	0.276
Micro Melt 23	7.987	0.005	3276	5.77	5940	20.00	85763	219756	0.280
Micro Melt 30	8.032	0.000	3286	11.54	5933	11.54	86770	222000	0.278
Micro Melt A 11LVC	7.444	0.002	3446	23.09	6126	11.54	88437	224223	0.267
Micro Melt A11	7.386	0.002	3453	11.54	6150	17.32	88082	223684	0.269
T 15 Spray formed	8.150	0.000	3332	26.83	5920	20.00	90487	229471	0.267
ESP 23	7.635	0.000	3253	23.09	6053	11.54	80809	209568	0.296
1.2999	7.853	0.001	3086	11.54	5900	0.00	74823	196263	0.311
1.2766	7.808	0 002	3000	20.00	5760	20.00	70274	184622	0.313

Appendix: B

Sample name: 1.3243

Analysed composition: 0.91C-4.10Cr-4 80Mo-0.23Ni-1.80V-6.10W-4.90Co

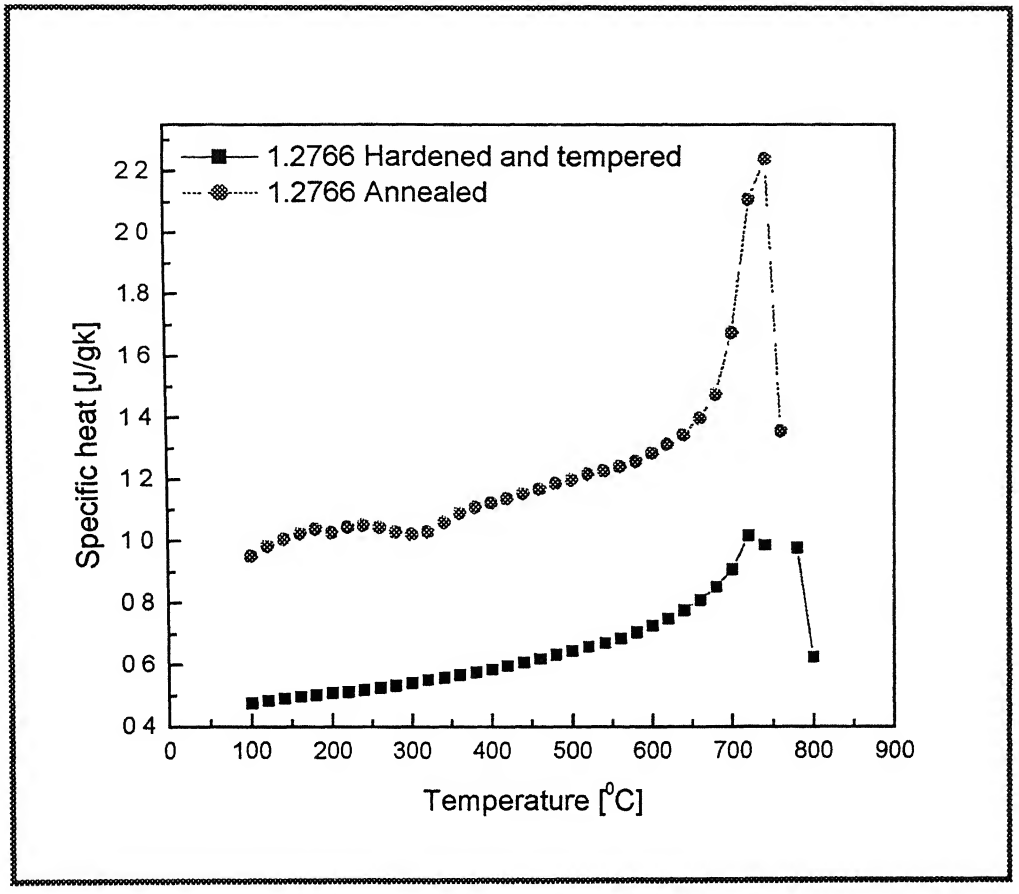
Condition: Annealed and hardened and tempered



Sample name: 1.2766

Analysed composition: 0.34C-1 76Cr-0.38Mo-3.86Ni-0.02V

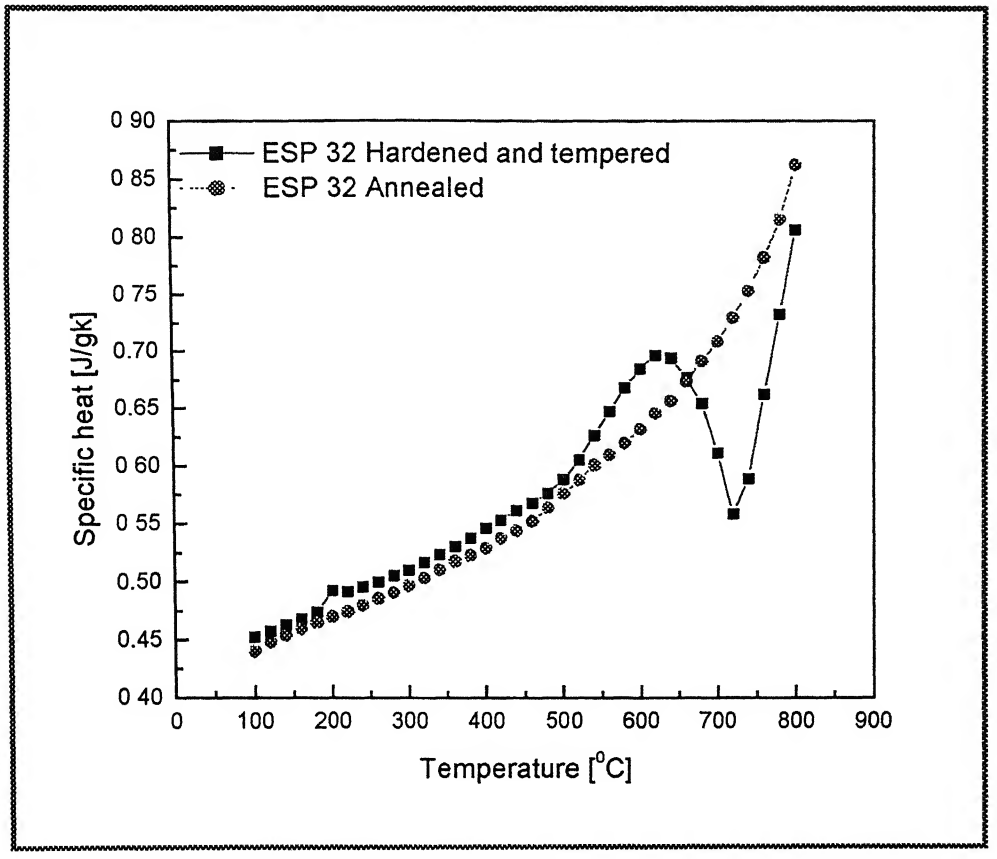
Condition: Annealed and hardened and tempered



Sample name: ESP 32

Analysed composition: 1.80C-3.89Cr-3.93Mo-0.12Ni-4.69V-9.26W-9.84Co-1.24Nb

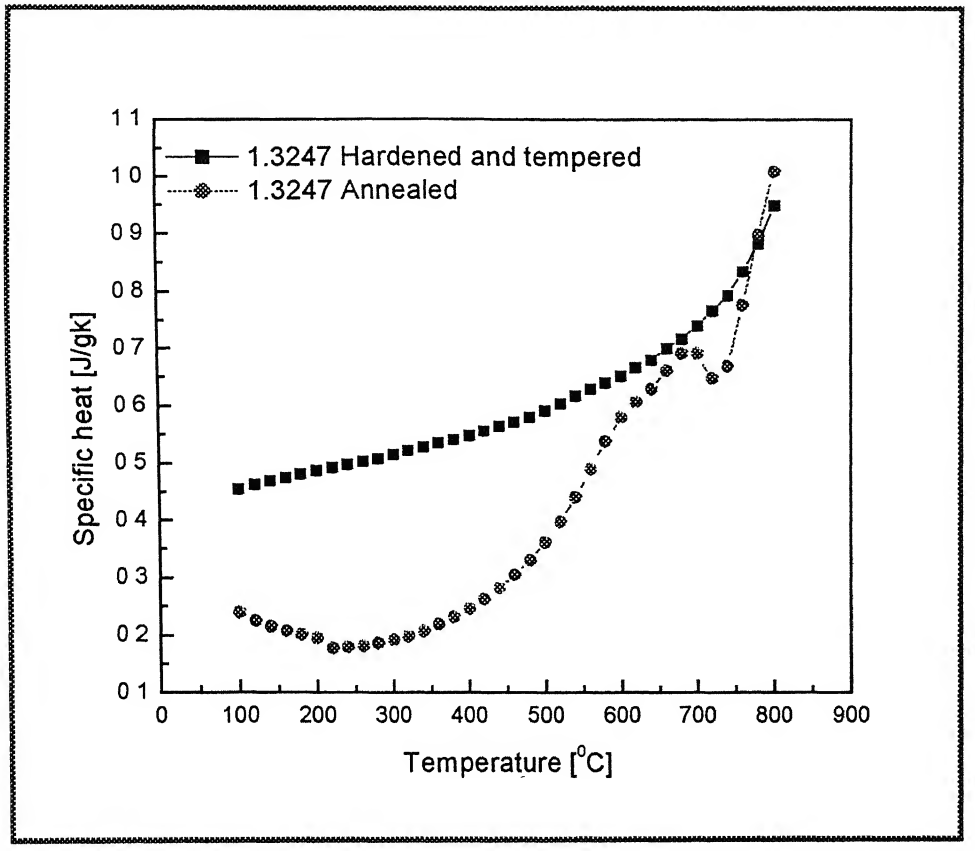
Condition: Annealed and hardened and tempered



Sample name: 1.3247

Analysed composition: 1.07C-3.90Cr-9.20Mo-0.13Ni-1.21V-1.40W-7.80Co

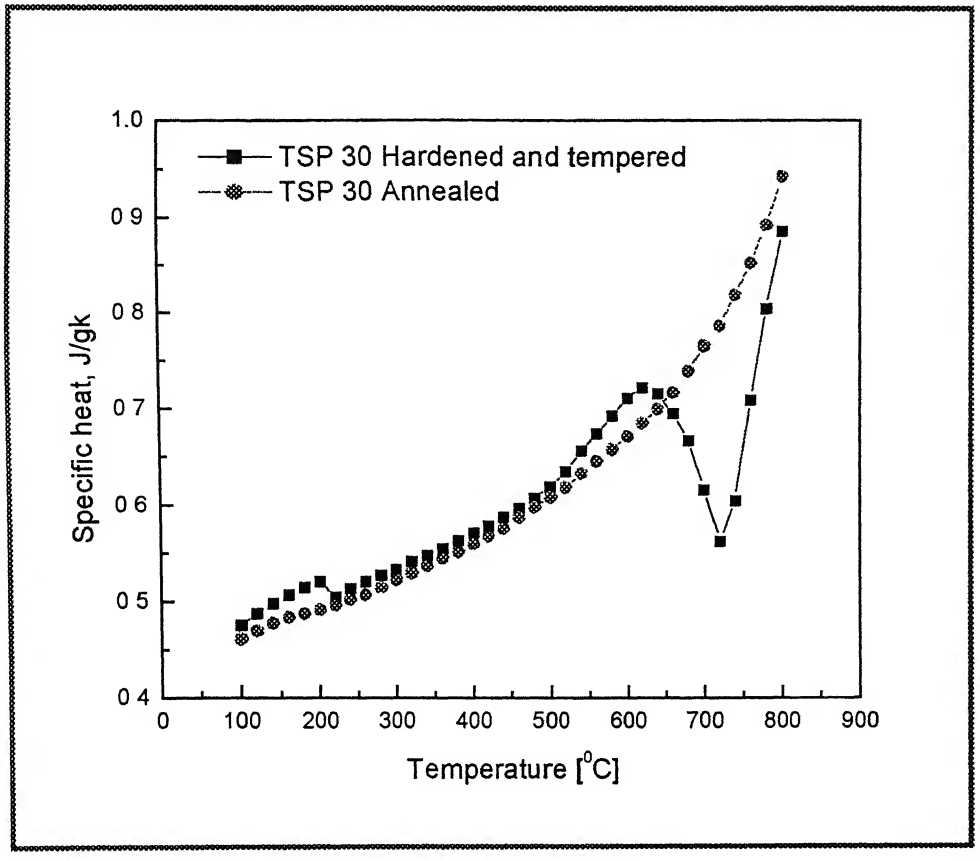
Condition: Annealed and hardened and tempered



Sample name: TSP 30

Analysed composition: 1.29C-4.23Cr-4.94Mo-0.29Ni-3 01V-6.51W-8.12Co

Condition: Annealed and hardened and tempered



Appendix: C

From potential energy versus distance curve we know that, at very large separation r, U is zero and as r is decreased, *U* decreases, goes through a minimum and then increases (fig. 1).

Let us approximate the potential energy curve by the equation:

$$U(r) = \frac{-A}{r^m} + \frac{B}{r^n} \tag{1}$$

This potential energy was also used to describe covalent bonds.

If r_0 and U_b (r_0 equilibrium interatomic spacing and U_b binding energy) are known, one can determine the constants A and B in the following way. At the minimum potential energy point:

$$F\big|_{r_o} = \left.\frac{dU}{dr}\right|_{r_0} = 0 \qquad \text{and} \qquad u(r_0) = -U_b \tag{2}$$

This with substitution to equation 13.8.1 and its derivative allows us to find that.

$$A = \frac{n}{n-m} U_b r_0^m \qquad \text{and} \qquad B = \frac{m}{n-m} U_b r_0^n \tag{3}$$

Substitution of A and B in equation 13 8.1 results in the following expression for U:

$$U(r) = \frac{U_b}{n-m}\left[-n\left(\frac{r_0}{r}\right)^m + m\left(\frac{r_0}{r}\right)^n\right] \tag{4}$$

Using the above equation, the stiffness of the bond S is given as follows:

$$S_0 = \left.\frac{dF}{dr}\right|_{r_0} = \left.\frac{d^2U}{dr^2}\right|_{r_0} = \frac{nm}{r_0^2} U_b \tag{5}$$

The elastic constant E (Young's modulus) can now be calculated as:

$$E = \left.\frac{d\sigma}{d\varepsilon}\right|_{\varepsilon=0} = \left.\frac{d\frac{F}{r_0^2}}{d\frac{r-r_0}{r_0}}\right|_{r_0} = \left.\frac{1}{r_0}\frac{dF}{dr}\right|_{r_0} = \frac{S_0}{r_0} = \left.\frac{1}{r_0}\frac{dU^2}{dr^2}\right|_{r_0} = \frac{nm}{r_0^3}U_b \qquad (6)$$

We can conclude that materials with high binding energies and small interatomic spacing, lead to high Young's modulus.

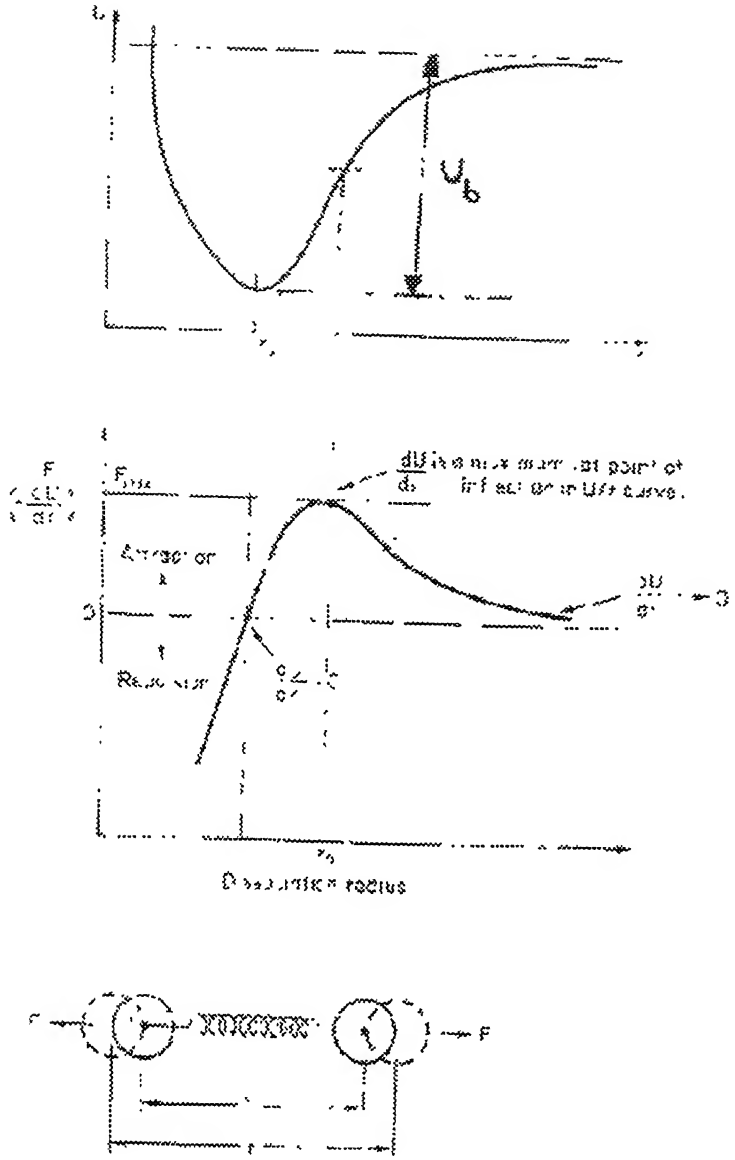


Fig. 1: Note that the force F is zero at the equilibrium separation r_0; if the atoms are pulled apart by the distance $(r-r_0)$, a force appears so as to resist this pulling. Note the sign notation for U and F=dU/dr. An attractive force is here taken as positive, whereas a repulsive force is taken as negative. Similarly a negative U defines energy that you need to provide to move the atoms apart (i.e. at infinity where U=0), whereas positive U corresponds to energy that you get back when you take the atoms to infinity. The stiffness S_0 of the bond is given as $S_0 = \left.\frac{dF}{dr}\right|_{r_0} = \left.\frac{d^2U}{dr^2}\right|_{r_0}$.

Appendix: D

Table 1: Comparison of elastic properties measured at IWK and IZEP

Sample name	Location	Transversal Velocity (m/s)	Longitudinal velocity (m/s)	G Modulus (N/mm²)	E Modulus (N/mm²)	ν Poisson's ratio
T 15 Spray formed	IWK	3332	5920	90487	229471	0.267
	IZFP	3309	6020	89238	229034	0.283
MicroMelt A 11	IWK	3453	6150	88082	223684	0.269
	IZFP	3500	6200	90478	229073	0.265
MicroMelt A 11 LVC	IWK	3446	6126	88437	224223	0.267
	IZFP	3465	6200	89374	227534	0.272
MicroMelt 30	IWK	3286	5933	86770	222000	0.278
	IZFP	3325	6004	88798	227116	0.278
MicroMelt 23	IWK	3276	5940	85763	219756	0.280
	IZFP	3326	6000	88354	225867	0.278
MicroMelt M 4	IWK	3300	5940	86471	220793	0.276
	IZFP	3320	6000	87517	223933	0.279
1.2379	IWK	3226	5973	79824	206599	0.293
	IZFP	3290	6014	82977	213493	0.286
CPM 3V	IWK	3206	5980	78560	203968	0.297
	IZFP	3220	6020	79214	205817	0.299
CPM 10V	IWK	3466	6186	88643	225362	0.270
	IZFP	3510	6334	90873	232341	0.278
CPM Re X M4	IWK	3320	5980	87188	222410	0.275
	IZFP	3328	6000	87607	223894	0.277

Table 1: Contiuned

CPM M 4	IWK	3313	5956	86719	221304	0.275
	IZFP	3306	6000	86333	221287	0.281
CPM T 15	IWK	3280	5876	87743	223507	0.273
	IZFP	3315	6030	89617	230039	0.283
1.3343	IWK	3166	5840	80989	209216	0.291
	IZFP	3200	5838	82698	212530	0.284
1.3344	IWK	3293	5893	86873	221164	0.272
	IZFP	3266	5970	85430	219806	0.286
TSP 5	IWK	3326	5976	89507	228264	0.275
	IZFP	3340	6075	90215	231569	0.283
ESP 4	IWK	3260	5966	84761	218212	0.286
	IZFP	3290	6030	86322	222369	0.288
1.3247	IWK	3166	5826	79791	205924	0.290
	IZFP	3166	6000	79791	208588	0.307
ASP 30	IWK	3273	5900	86082	219968	0.277
	IZFP	3310	6040	88021	226276	0.285
TSP 8 Cr 18	IWK	3560	6366	93725	238539	0.271
	IZFP	3557	6479	93563	240270	0.284
1.2888	IWK	3253	5880	85248	218131	0.279
	IZFP	3290	5909	87177	222363	0.275

Table 1: Continued

1.2889	IWK	3146	5786	77083	198822	0.289
	IZFP	3290	5886	84265	214510	0.272
TSP 30	IWK	3260	5920	85385	218986	0.282
	IZFP	3335	6080	89355	229606	0.284
TSP 23	IWK	3186	5960	81320	211399	0.299
	IZFP	3250	6030	84584	219116	0.295
CPM 15V	IWK	3526	6273	89698	227639	0.268
	IZFP	3650*	6503*	96081*	244056*	0.270*
TSP 1	IWK	3106	5926	74956	196485	0.308
	IZFP	3193	-	79176	-	-
1.3243	IWK	3180	5806	81869	210537	0.285
	IZFP	3200	-	82903	-	-
TSP 4	IWK	3273	6133	84939	220923	0.300
	IZFP	3412*	6220	92284	237072*	0.284*
1.2343	IWK	2993	5730	69383	182096	0.314
	IZFP	-	-	-	-	-
1.2344	IWK	2906	5846	65258	174455	0.336
	IZFP	-	-	-	-	-
1.2367	IWK	2964	5808	68526	181427	0.323
	IZFP	-	-	-	-	-
101≈2343	IWK	2906	5773	65942	175433	0.329
	IZFP	3251*	5940*	82491*	212192*	0.286*
T 15 HIP	IWK	3330	5956	90448	230230	0.272
	IZFP	3306	5081*	89142	202050*	0.133*

Table 1: Continued

ESP 32	IWK	3386	6000	92463	234124	0.265
	IZFP	3373	6479*	91711	241023	0.314*
ESP 23	IWK	3253	6053	80809	209568	0.296
	IZFP	3285	6224	82391	215363	0.306
2999	IWK	3086	5900	74823	196263	0.311
	IZFP	3240	5948	82437	212524	0.289
TSP 8	IWK	3393	6246	85815	221516	0.290
	IZFP	3508	6351	91458	234223	0.280
1.2365	IWK	2980	5844	69454	183947	0.323
	IZFP	3259*	5999*	83067*	213293*	0.283*

Appendix: E

Sample name: TSP 30

Analysed composition: 1.29C-4.23Cr-4.94Mo-0.29Ni-3.01V-6.51W-8.12Co

Condition: Annealed

T [°C]	C_p [J/gk]
100	0 462
120	0 470
140	0 478
160	0 484
180	0 488
200	0 492
220	0 496
240	0 502
260	0 507
280	0.515
300	0 523
320	0 530
340	0 537
360	0 545
380	0 552
400	0 560
420	0.568
440	0 576
460	0 588
480	0 598
500	0 609
520	0 619
540	0 633
560	0 646
580	0 658
600	0 671
620	0 685
640	0.700
660	0.717
680	0 739
700	0 765
720	0.786
740	0 818
760	0.852
780	0 892
800	0 942

Sample name: 1.3247

Analysed composition: 1.07C-3.90Cr-9.20Mo-0.13Ni-1.21V-1.40W-7.80Co

Condition Annealed

T [°C]	C_p [J/gk]
100	0 45471
120	0 46262
140	0 46941
160	0 47522
180	0 48121
200	0 48693
220	0 49187
240	0 49774
260	0 50307
280	0 50843
300	0 51603
320	0 52263
340	0.52926
360	0 53596
380	0.54236
400	0 54907
420	0 55730
440	0 56512
460	0 57250
480	0 58097
500	0 59187
520	0 60375
540	0 61710
560	0 62975
580	0 64037
600	0 65214
620	0 66746
640	0 68006
660	0 70025
680	0 71708
700	0 74094
720	0.76676
740	0 79378
760	0 83479
780	0.88233
800	0 94789

Sample name: ESP-32

Analysed composition 1 80C-3.89Cr-3 93Mo-0.12Ni-4.69V-9.26W-9.84Co-1.24Nb

Condition Annealed

T [°C]	C_p [J/gk]
100	0 44071
120	0 44822
140	0 45458
160	0 46001
180	0 46516
200	0 47007
220	0 47472
240	0 48007
260	0 48588
280	0 49109
300	0 49710
320	0 50361
340	0 51104
360	0 51816
380	0 52305
400	0 52972
420	0 53798
440	0 54488
460	0 55306
480	0 56457
500	0 57691
520	0 58835
540	0.60160
560	0 61057
580	0 62114
600	0 63303
620	0 64658
640	0 65779
660	0 67484
680	0 69222
700	0 70900
720	0 72989
740	0 75350
760	0 78243
780	0 81520
800	0.86215

Sample name 1 2766

Analysed composition: 0.34C-1 76Cr-0.38Mo-3.86Ni-0.02V

Condition Annealed

T [°C]	C_p [J/gk]
100	0 47696
120	0 48548
140	0 49308
160	0 49871
180	0 50465
200	0 50977
220	0 51487
240	0 52044
260	0 52687
280	0 53520
300	0 54342
320	0 55206
340	0 56024
360	0 56913
380	0 57852
400	0 58829
420	0 59941
440	0 61019
460	0 62297
480	0 63563
500	0 64856
520	0 66126
540	0 67417
560	0 68947
580	0 70761
600	0 73030
620	0 75231
640	0 77888
660	0 81222
680	0 85427
700	0 91114
720	1 02021
780	0 98160
800	0 62881

Sample name: 1.3243

Analysed composition. 0 91C-4.10Cr-4 80Mo-0.23Ni-1.80V-6.10W-4.90Co

Condition: Annealed

T [°C]	C_p [J/gk]
100	0 45524
120	0 46378
140	0 47228
160	0 48003
180	0 48926
200	0 49440
220	0 49782
240	0 50259
260	0 50553
280	0 51463
300	0.52154
320	0 52992
340	0 53706
360	0 54465
380	0 55144
400	0 56036
420	0 56869
440	0 57720
460	0 58777
480	0.59910
500	0 61124
520	0 62295
540	0 63528
560	0 64692
580	0.65941
600	0 67362
620	0 69056
640	0.70729
660	0.72856
680	0 75241
700	0.77961
720	0.80866
740	0 84777
760	0.89334
780	0 95463
800	1 03894

Sample name. TSP 30

Analysed composition. 1 29C-4 23Cr-4.94Mo-0.29Ni-3.01V-6.51W-8.12Co

Condition. Hardened and tempered

T [°C]	C_p [J/gk]
100	0 47575
120	0 48786
140	0 49779
160	0 50646
180	0 51472
200	0 52049
220	0 50502
240	0 51350
260	0.5210
280	0 52737
300	0 53345
320	0 54137
340	0 54792
360	0 55470
380	0 56313
400	0 57116
420	0 57854
440	0 58758
460	0 59686
480	0 60758
500	0 61944
520	0 63506
540	0 65606
560	0 67385
580	0 69197
600	0 71059
620	0 72224
640	0 71503
660	0 69489
680	0 66757
700	0.61691
720	0 56345
740	0.60532
760	0 70900
780	0.80407
800	0.88520

Sample name 1.3247

Analysed composition: 1 07C-3 90Cr-9 20Mo-0.13Ni-1.21V-1.40W-7.80Co

Condition: Hardened and tempered

T [°C]	C_p [J/gk]
100	0 24001
120	0 22572
140	0 21530
160	0 20838
180	0 20189
200	0 19616
220	0 17797
240	0 17995
260	0 18150
280	0.18659
300	0 19193
320	0.19895
340	0 20823
360	0 21985
380	0 23255
400	0 24661
420	0 26357
440	0 28321
460	0.30503
480	0 33068
500	0.36125
520	0 39811
540	0.44183
560	0.49075
580	0.53966
600	0 58093
620	0 60779
640	0.62929
660	0 66177
680	0.69144
700	0 69200
720	0 64820
740	0.66878
760	0.77697
780	0.89814
800	1 00776

Sample name: ESP 32

Analysed composition: 1.80C-3.89Cr-3 93Mo-0.12Ni-4.69V-9.26W-9.84Co-1.24Nb

Condition: Hardened and tempered

T [°C]	C_p [J/gk]
100	0.45273
120	0.45806
140	0.46317
160	0 46774
180	0 47417
200	0 49259
220	0 49242
240	0 49614
260	0 50057
280	0 50562
300	0 51091
320	0 51727
340	0 52417
360	0 53126
380	0 53894
400	0 54671
420	0.55430
440	0.56236
460	0.56884
480	0.57708
500	0 58901
520	0 60612
540	0 62783
560	0 64910
580	0.66928
600	0 68573
620	0 69744
640	0.69471
660	0 67813
680	0.65575
700	0 61238
720	0 55964
740	0.59030
760	0.66356
780	0.73348
800	0.80695

Sample name. 1.2766

Analysed composition: 0.34C-1.76Cr-0.38Mo-3.86Ni-0.02V

Condition: Hardened and tempered

T [°C]	C_p [J/gk]
122	0 95093
142	0 98235
162	1 00492
182	1 02492
202	1 03888
222	1 02652
242	1 04437
262	105060
282	1 04492
302	1 03035
322	1 02143
342	1 02979
362	1 06075
382	1 09126
402	1 11134
422	1 12514
442	1 13971
462	1 15469
482	1 17056
502	1 18826
522	1 20073
542	1 21940
562	1.22856
582	1 24375
602	1 25942
622	1 28867
642	1 31580
662	1 34729
682	1 40058
702	1.47881
722	1 67731
742	2 10807
762	2 23884
782	1 36003

Sample name. 1.3243

Analysed composition: 0.91C-4.10Cr-4.80Mo-0.23Ni-1 80V-6.10W-4.90Co

Condition: Hardened and tempered

T [°C]	C_p [J/gk]
100	0 47200
120	0 48189
140	0 49005
160	0 49782
180	0 50253
200	0 49456
220	0 50564
240	0 51320
260	0 52088
280	0 52752
300	0 53454
320	0 54139
340	0.54850
360	0.55590
380	0 56401
400	0 57257
420	0.58123
440	0.59103
460	0 60054
480	0 61128
500	0 62559
520	0 63996
540	0 65900
560	0 67786
580	0 69225
600	0 69050
620	0 66486
640	0.63472
660	0 63220
680	0 65200
700	0.67180
720	0 65911
740	0.62745
760	0.66813
780	0.78444
800	0.95176

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